Supplementary Information
On the structure of water and chloride ion interactions with a peptide backbone in solution

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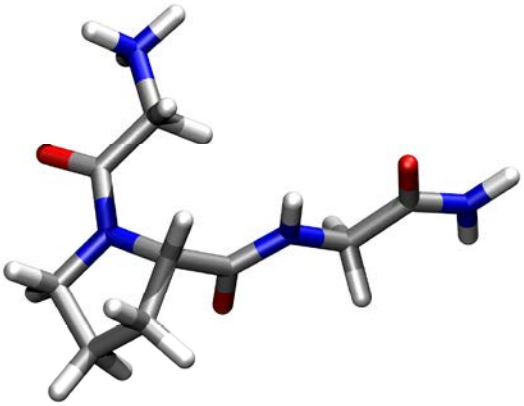
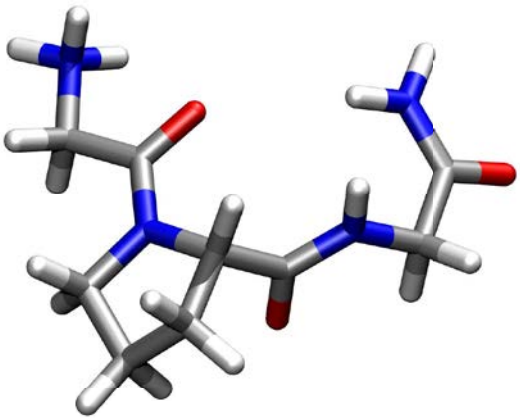


cis GPG



trans GPG

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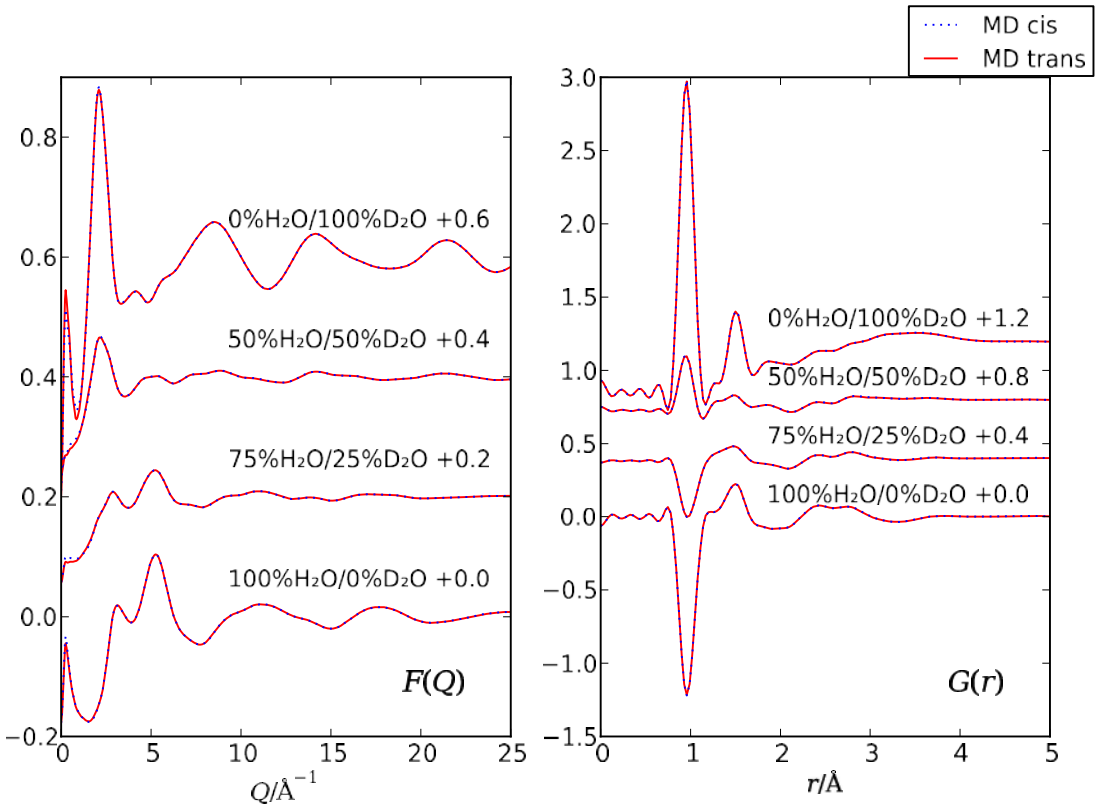
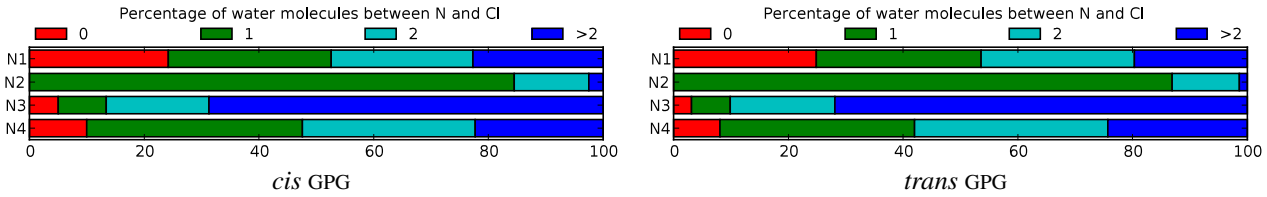
1 Diffraction patterns

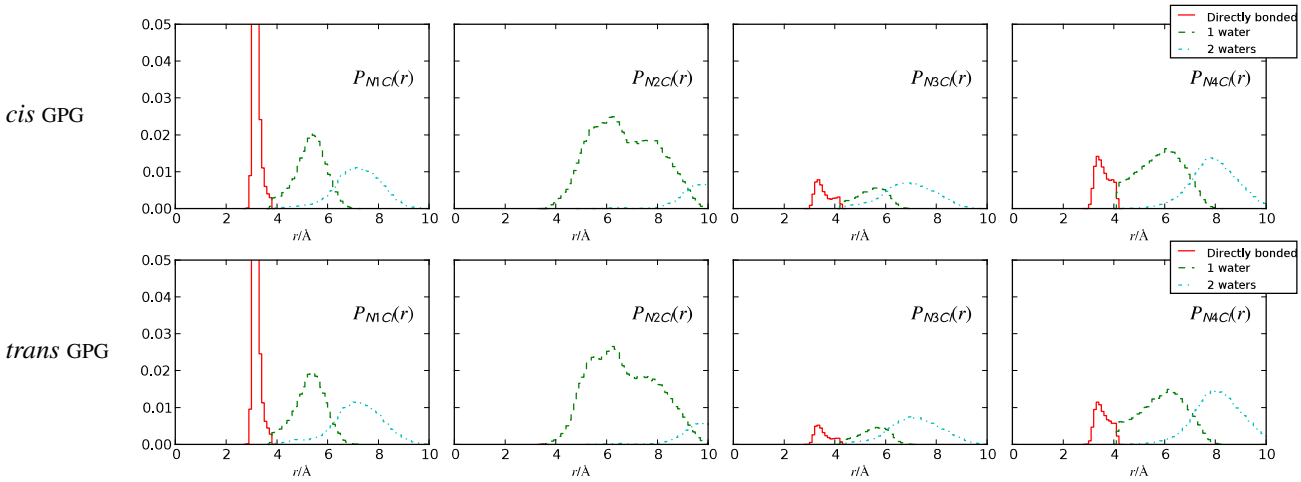


The calculated $F(Q)$ and $G(r)$ of *cis* and *trans* GPG MD simulations are virtually indistinguishable. These quantities are weighted sums of average distances.

2 Water mediation N–Cl



The distribution of percentages of water molecules that are between a given nitrogen and the next chloride ion is virtually unaffected by the conformational state of GPG.



The distance distributions of chloride ions that are either in direct contact with a given nitrogen atom or are removed by 1 or 2 water molecules is not sensitive to the *cis trans* isomerisation.

3 Chloride mediation N–N

	N1	N2	N3	N4
N1	5%	7%	2%	12%
N2	**25%**	7%	0%	11%
N3	**1%**	**3%**	0%	1%
N4	**4%**	**4%**	**5%**	6%

cis GPG

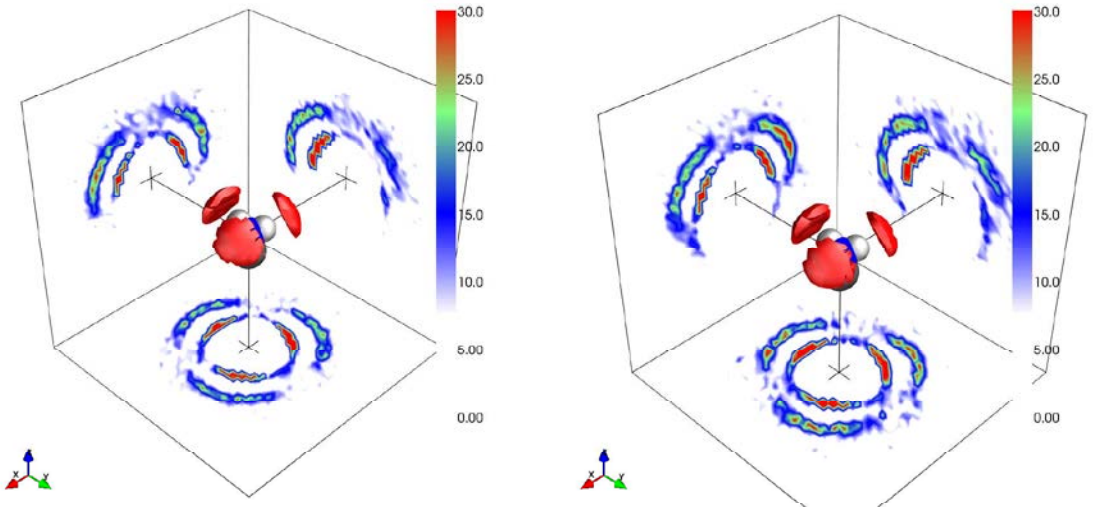
	N1	N2	N3	N4
N1	6%	8%	1%	12%
N2	**29%**	9%	0%	11%
N3	**0%**	**3%**	0%	1%
N4	**2%**	**4%**	**4%**	5%

trans GPG

The fraction of Cl^- ions that are within up to two water molecules of a nitrogen Ni and simultaneously within up to two water molecules of a different Nj. Neither the inter- (normal face) nor intra-molecular (bold face) numbers change appreciable. The biggest difference between *cis* and *trans* can be seen in the intramolecular N1–N2 term which is slightly more populated in the *trans* state.

4 Spatial Distribution Maps

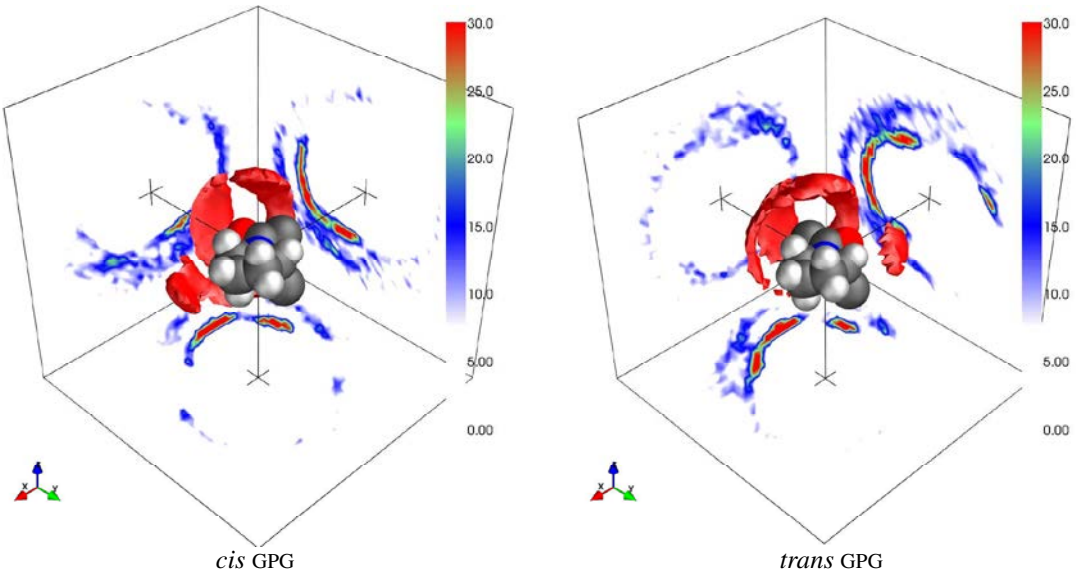
N1



cis GPG *trans* GPG

There is no visible difference in the chloride distribution around the NH_3^+ group.

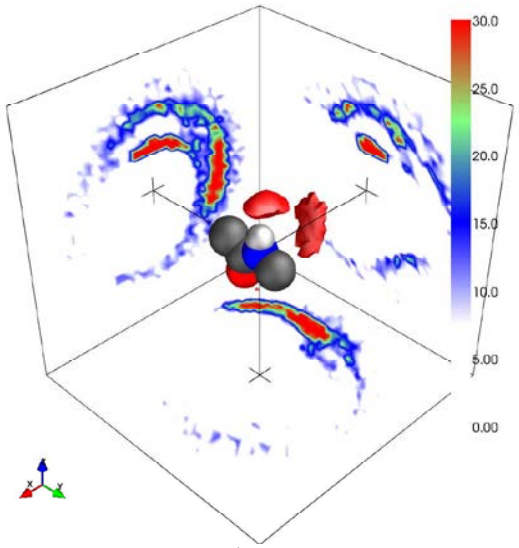
N2



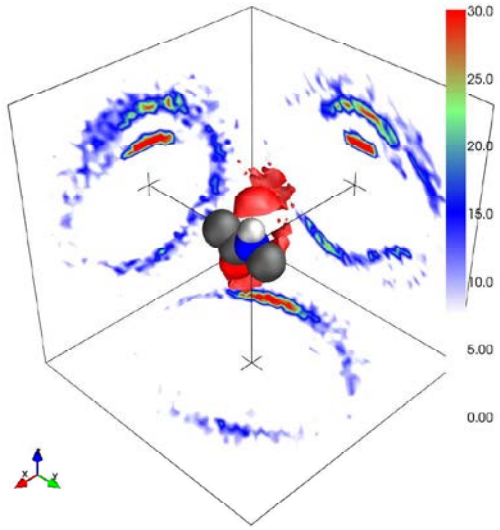
cis GPG *trans* GPG

As discussed in the main text, a small patch of chloride density is at a different position in the *cis* and *trans* state of GPG. While it is in front of the proline ring in the *cis* state, it can be found above the continuation of the backbone in *trans* GPG.

N3



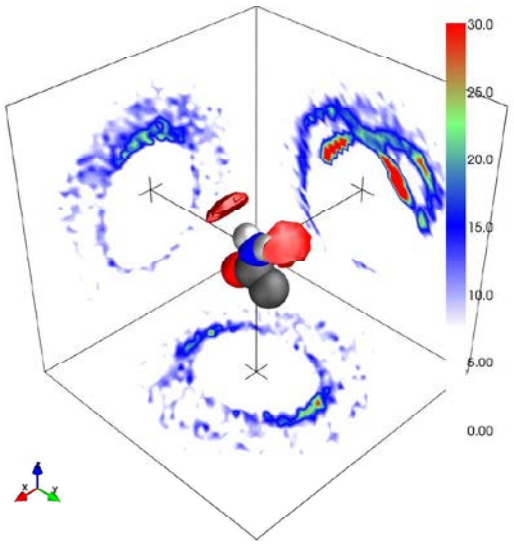
cis GPG



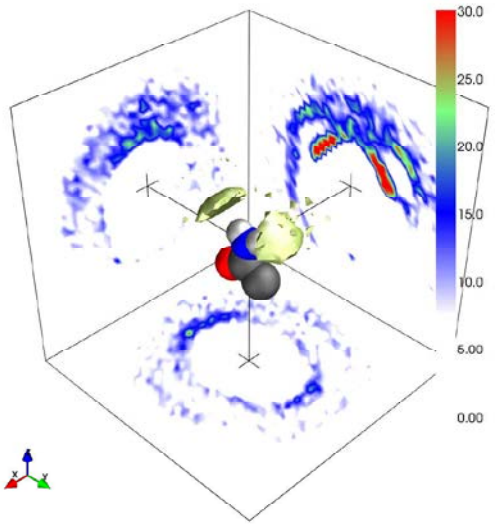
trans GPG

Although the cuts through the chloride density look somewhat different between *cis* and *trans* GPG, the three-dimensional picture shows that there is no qualitative change in the distribution, only a small shift of the high density areas. This small shift brings about that they are well visible in the cuts of the *cis* state while they are not directly in the cut plane in the *trans* state.

N4



cis GPG



trans GPG

The positions of high chloride density are the same around the NH_2 groups of *cis* and *trans* GPG. Both cuts contain the top 5% of chloride density. As indicated by the colour of the isosurface, this is achieved at slightly different contourlevels. The cuts through the chloride density show however that this difference is not significant.