Supporting information

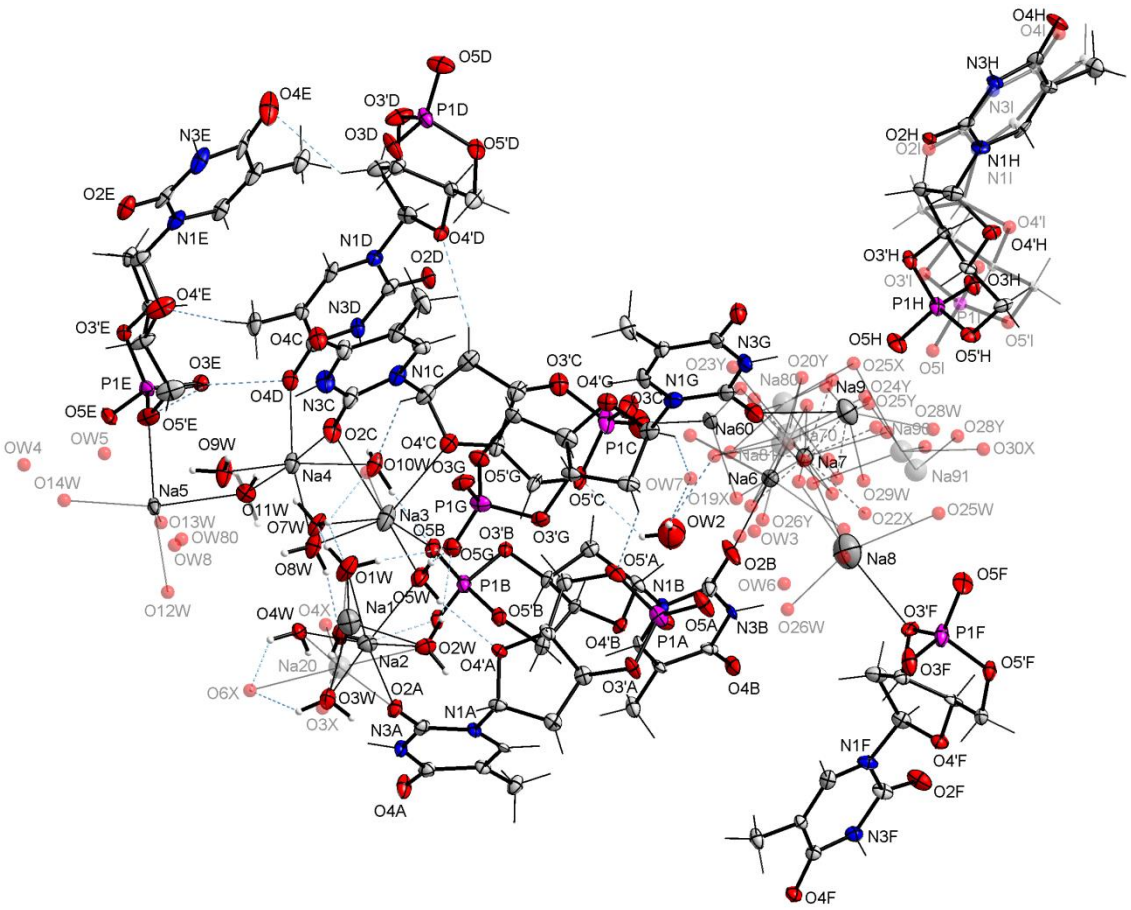

Figure S1 Asymmetric unit of (**II**), showing the atom-numbering scheme (for P, Na, N and selected O atoms) and symmetry–independent hydrogen bonds (blue dashed lines). Displacement ellipsoids are shown at the 30% probability level. Two positions of the disordered cdTMP^{-} anion *H*/*I* are shown: with higher occupancy factors – black bonds and labels; with lower s.o.f.s – transparent bonds and atoms (shown as spheres) and grey labels. Transparent spheres (and grey labels) represent partially occupied atoms, which were refined isotropically.

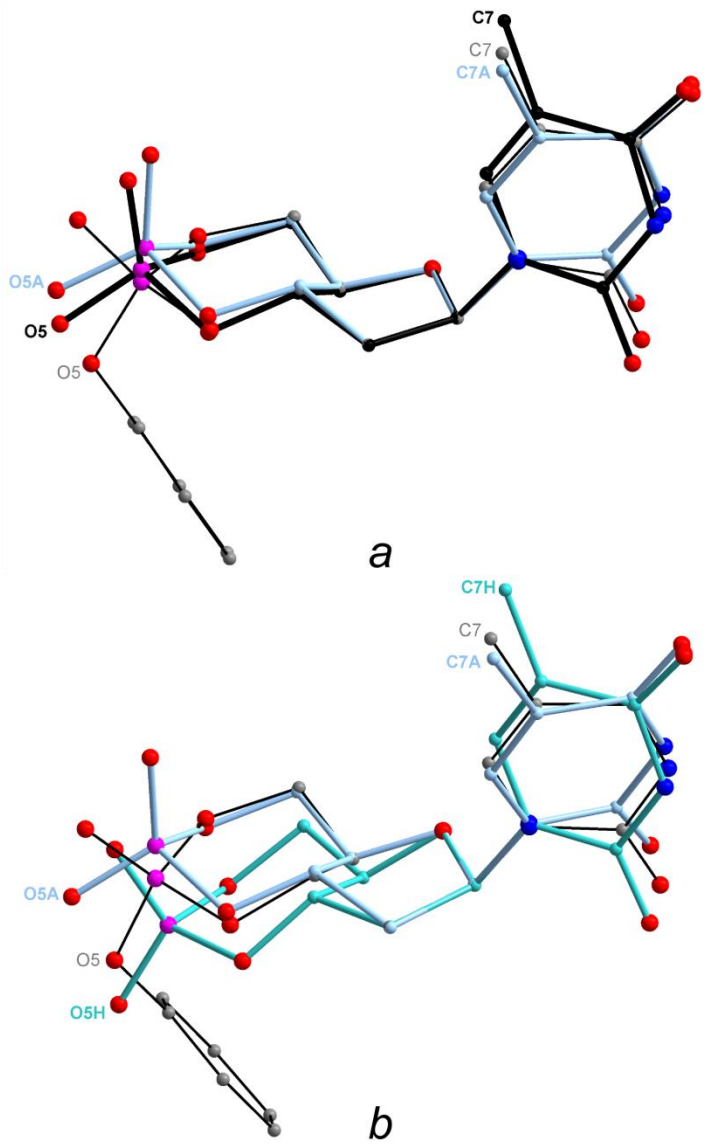

Figure S2 Comparison of the geometry of cdTMP^{-} anions, showing (***a***) the effect of different deformation of the O/P/O/C/C/C ring (when the sugar ring is puckered in the same way; (**I**) vs. (**II**)-*A*), and (***b***) the effect of different sugar puckering and O/P/O/C/C/C ring deformation ((**II**)-*A* vs. (**II**)-*H*). Colour scheme as in Fig. 3: (**I**) – thick black bonds; crystallographically independent *A* and *H* from (**II**) – colour bonds; cdTMP(Ph) (Nelson *et al.*, 1987) – thin black bonds. The common reference points are O4′, C1′ and C2′ atoms.

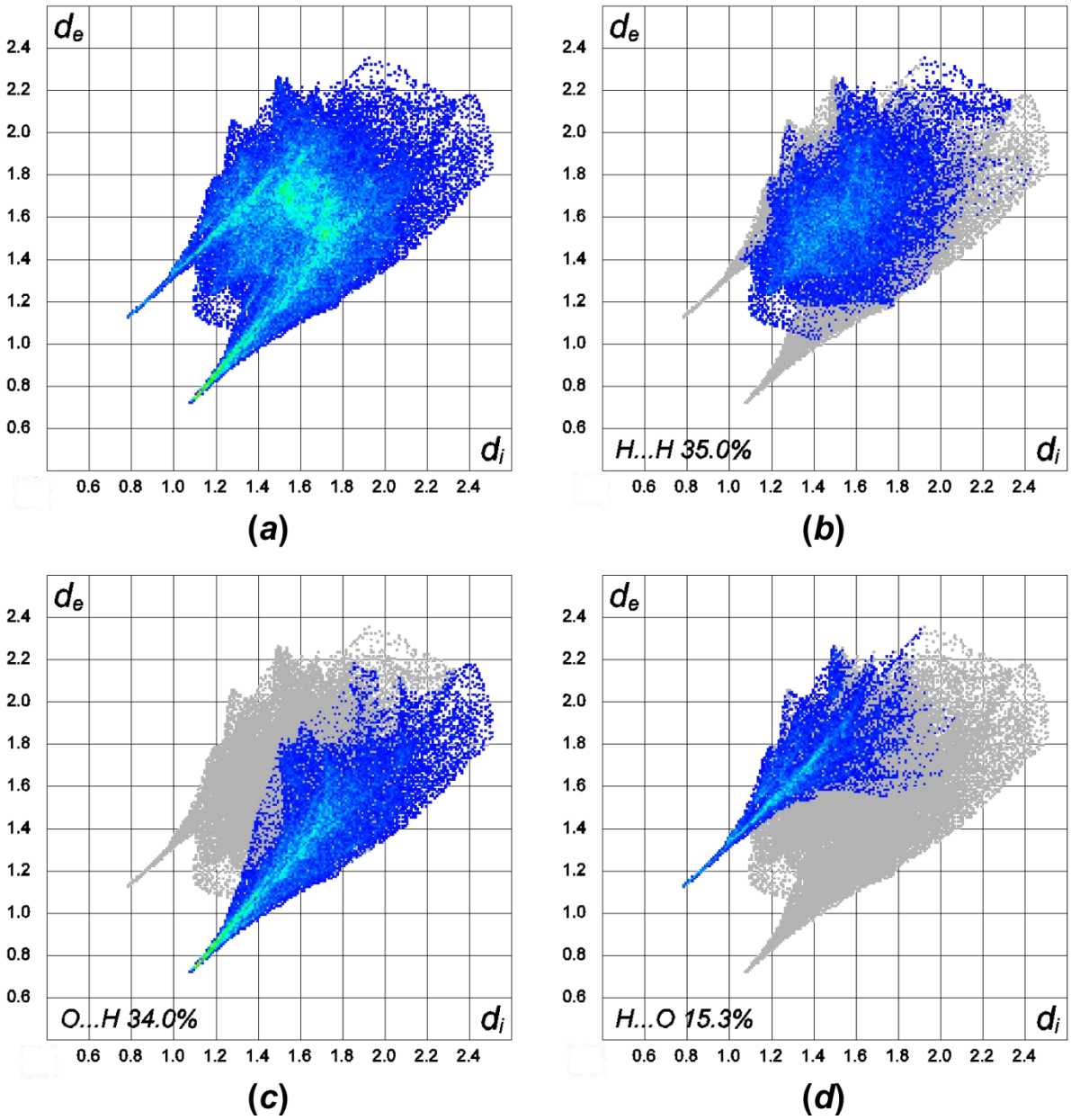

Figure S3 2D fingerprint plots for cdTMP^{-} in (**I**): (*a*) – all contacts; (*b*)–(*d*) – the main types of contacts and their contribution to the surface area.