Ring-Stacking and Ring-Laddering in the Organic Solid State

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The ring-stacking and ring-laddering concepts of structural inorganic chemistry[1-6] may be applied to rationalise motifs observed for secondary ammonium halides R_2NH_2X (X = Cl, Br) in the organic solid state.

General examination of the directional preferences of $N^+\cdots X^-$ contacts in 166 crystal structures confirms that the shortest contacts (3.0–3.2 and 3.2–3.4 Å, X = Cl, Br) are N^+–$H\cdots X^-$ hydrogen bonds lying approximately along the directions of the N^+–H bond vectors. The next shortest $N^+\cdots X^-$ contacts display two preferred directions of approach: i) contacts in the distance range 3.2–3.5 (X = Cl) and 3.2–3.9 Å (X = Br) lie close to the H–N^+–H plane, along the direction of the bisector of the H–N^+–H angle; ii) contacts in the distance range 4.0–4.2 (X = Cl) and 4.0–4.4 Å (X = Br) lie close to the H–N^+–H plane, along the direction of an axis extending to the backside of one the N^+–H bonds. Both directions of approach lead frequently to association of $R_2NH_2^+X^-$ ion pairs into laddered motifs. Stacking association is also observed, giving rise in one case to discrete cubanes and in several other cases to extended stacked-cube arrangements.

In each case, the distribution of $N^+\cdots X^-$ contacts reflects a balance between the directional properties of the N^+–$H\cdots X^-$ hydrogen bonds and (primarily steric) interactions between the R groups of the organic moieties. The ladder and stack motifs of the organic ammonium halides are in many cases directly comparable to those in alkali-metal amides, $[R_2NM]_n$, and information derived from the extensive organic sample provides insight into the motifs adopted by inorganic complexes.

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