

s13.m36.o1 **Ring-Stacking and Ring-Laddering in the Organic Solid State.** Andrew D. Bond, *Department of Chemistry, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark. E-mail: adb@chem.sdu.dk*

Keywords: Database Analysis; Ring-Stacking/Ring-Laddering; Hydrogen Bonding

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 $N^+...X^-$ contacts in 166 crystal structures confirms that the shortest contacts (3.0–3.2 and 3.2–3.4 Å, $X = Cl, Br$) are $N^+...X^-$ contacts displaying two preferred directions of approach: i) contacts in the distance range 3.2–3.5 Å ($X = Cl$) 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 Å ($X = Cl$) 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 of the N^+-H bonds. Both directions of approach lead frequently to association of $R_2NH_2^+X^-$ ion pairs into ladder motifs. Stacking association is also observed, giving rise in one case to discrete cubanes and in several other cases to extended stacked-cube arrangements.

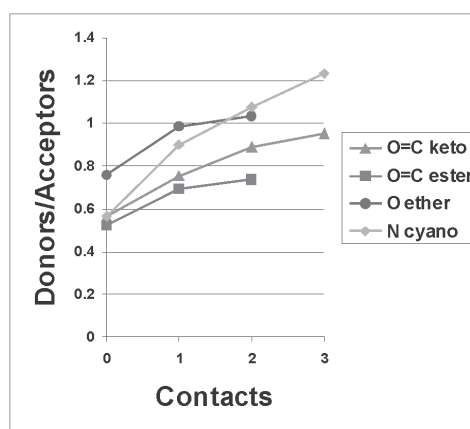
In each case, the distribution of $N^+...X^-$ contacts reflects a balance between the directional properties of the $N^+-H...X^-$ hydrogen bonds and (primarily steric) interactions between the R groups of the organic moieties. The ladder and stack motifs of the organic ammonium halides are in many cases 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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s13.m36.o2 **CSDContact: a Database of Hydrogen Bond Contacts for Chemical Groups.** Sam Motherwell & Lourdes Infantes, *Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge, CB2 1EZ, UK. E-mail: motherwell@ccdc.cam.ac.uk*

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Much work has already been carried on H-bond studies using the Cambridge Structural Database (CSD)[1], identifying motifs and geometric parameters. However there are limitations imposed by the standard search software, ConQuest, which make it difficult or impossible to get statistics on particular chemical groups, such as the average number of H-bond contacts per atom, or per group, for selected molecules with specified exact proportions of chemical groups, or a donor/acceptor ratio. A new methodology has been used, where the PLUTO program has been enhanced to batch-process a selected set of CSD entries generating all required non-bonded contacts. Output files are used to create a Microsoft Access database, which has a flexible query language to enable selection of groups, donor/acceptor ratios and create histogram data on contacts. A set of 41055 CSD accurate structures was used, which contain at least one H-bond donor. Atoms were assigned to one of 108 chemical groups. We calculated values for the sterically accessible surface [2] (AS) for atoms other than C,H, molecular volume, and the H-bonded graph set symbols. Some example studies will be presented, showing how the number of H-bond contacts per atom in a given chemical group is positively correlated with increasing AS, and increasing donor/acceptor ratio. The effect of limited selections of groups per molecule is also presented, where we observe preferred patterns and departures from the total sample statistics of average H-bonds per group.



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