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Charge density studies on halogen bonding interactions

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Research interest in “halogen bonding” interactions has been increasing in recent years because this directional and selective interaction is an effective tool in crystal engineering for designing functional solids [1]. Its applications in preferential nucleation [2], supramolecular architecture [1], molecular recognition [3] and solid-state synthesis [3] are well documented. Unlike H-atom bridge in conventional D-H...A, the halogen bridging D-Hal...O with both halogen and oxygen known for electronegative nature is of considerable interest. To gain more insight into halogen bonding interactions (C-Cl...O), we have carried out charge density studies on a model compound 2,5-dichloro-1,4-benzoquinone, having excellent C-Cl...O geometry [$d(\text{Cl}\cdots\text{O}) = 3.10 \text{ \AA}$, $\angle\text{C-Cl}\cdots\text{O} = 164.7^\circ$][4]. Charge density analysis is based on X-ray diffraction data (resolution $\sim 0.5 \text{ \AA}$) collected on a good quality crystal at 90 K. The intermolecular interactions were analyzed on Bader’s quantum theory [5]. Interestingly, the C-Cl bond was observed to be of the “closed shell” type. The bond critical point showed that C-Cl...O contact with magnitudes of $\rho(r)$ and $\tilde{N}^2\rho(r)$ indicating the interaction to be comparable with C-H...O interactions.

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Keywords: halogen bonding, charge density, topological analysis

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An organized protocol for weak C-H...X intermolecular bonding in the absence of a hydrogen bond

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Topological analyses from Charge Density Studies have shown many instances of weak C-H...X inter-(and intramolecular) interactions within a crystal. These have often been thought to be the consequence of accidentally fortuitous circumstances in the context of the larger forces operating in the crystal. However it is now appears, that in many instances, these weak C-H... interactions are part of a highly organized system. We report here the evidence found in a sequence of alkyl diammonium dithiocyanates. The thiocyanate ion (SCN⁻) has a strong hydrogen bond acceptor at the N and a less strong one

at the S atom. In addition the CN triple bond is a potent source for C-H... π interactions. We have examined the $(\text{NH}_3(\text{CH}_2)_n\text{NH}_3)^{2+}$ (SCN⁻)₂ (n= 0-6) as well as the corresponding N,N,N',N' tetramethyl-alkyl-diammonium dithiocyanate salts. In the simple ammonium salts there are three N-H donors for each (SCN⁻) anion which satisfies all the hydrogen bonding requirements of the N-H...NCS and N-H...SCN systems. With the tetramethyl salts however, there is only one N-H bond and in this case the N-H...NCS hydrogen bond is formed and methyl C-H bonds organize themselves in a very specific manner to replace the missing N-H...S interaction. In one instance we have examined the N,N'-ethylenediammonium (SCN⁻)₂. Here three of the four N-H bonds are used to form a bifurcated hydrogen bond to NCS and a linear N-H...S to the same (SCN⁻). The last N-H bond forms an N-H...N hydrogen bond to the second (SCN⁻) and the methyl C-H bonds organize themselves in a square pyramidal arrangement that almost exactly replaces the missing N-H...S interaction. The methylene C-H bonds meanwhile assume the role of the C-H... π interactions. This developing scenario will be shown over the full range of the sequence.

Keywords: intermolecular interactions, weak interactions, hydrogen bonds

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A study of electron momentum density distributions in polyethylene, polypropylene and polybutene

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We aim to obtain information about the ground state wave functions in highly oriented polyethylene (PE), polypropylene (PP) and polybutene (PB) via Compton profile (CP) measurements. CP is the twice integrated electron momentum density. Thus CP carries direct information about the ground state wave functions. The measurements were carried out by a Compton scattering spectrometer with a momentum resolution of 0.13 a.u. installed at ARNE1 beam line of the Photon Factory, KEK. Almost 100% oriented PE was obtained from Toyobo Co. (Dyneema) in a form of fiber. The oriented PP and PB specimens were prepared by stretching semi-oriented film at a proper temperature. Figure 1 shows the difference between the CP measured with along the direction of the carbon chain axis and that measured with perpendicular to the axis for PE, PP and PB. It is seen that the difference of CP on PE is modified by replacing one of H with CH₃ (PP) and CH₂-CH₃ (PB). These results are going to be analyzed in terms of the autocorrelation function which is a Fourier transform of the CP.

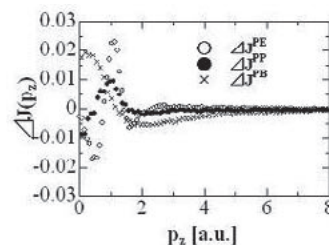


Fig. 1

Keywords: Compton profiles, polymer science, synchrotron X-rays