Rigid-rod shaped molecules are well-known for their tendency to form liquid crystalline phases. In order to probe the effect of substituents with differing electronic properties on liquid crystalline phase behaviour, a series of conjugated symmetric and unsymmetric (π-donor/acceptor) rigid-rod compounds composed of alternating aryl and alkylnyl groups have been prepared. The solid state single crystal structures of these bis(phenylethynyl)benzenes (BPEBs) and diphenyl acetylenes (tolans) have been determined with a view to understanding the relationship between packing in single crystals and thermotropic liquid crystalline phase behaviour.

Recently it has been observed that the halogens, Cl, Br and I form mutual recognition motifs with nitro groups.[1-3] Interactions of this type are of interest because of their potential to act as substructural building blocks in crystal engineering applications.[4]. The usefulness of X...O2N interactions for this purpose is critically dependent on our ability to predict their occurrence. In order to do that we must have some understanding of the nature and strength of the interaction.

A previous crystallographic database study of X...O2N interactions[1] revealed that there are three X...O2N bonding modes: a symmetric P type, a skew Q type and an asymmetric R type. However, the precise geometric and energetic differences between these three were not investigated further.

In view of the limited scope of the previous study and the recent improvements in the Cambridge Crystallographic Database System's[5] three dimensional search software it was felt that it was appropriate to perform a more complete analysis of the crystallographic results relating to X...O2N interactions and additionally, to obtain quantitative estimates of the interaction energies involved. The results of this study, together with relevant new structural data, will be presented.

References: