Carbyne: The rational synthesis of an sp-hybridized carbon allotrope

Carbon allotropes from sp$^3$-hybridized carbon (diamond) and sp$^2$-hybridized carbon (graphite, graphene, fullerenes, nanotubes) have well-established properties, many of which are technologically relevant. A carbon allotrope constructed from sp-hybridized carbon atoms (carbyne), on the other hand, remains rare and presents a challenging synthetic goal. In recent years, we have developed methods for the synthesis of symmetrical and unsymmetrical polyynes via the rearrangement of suitably functionalized carbenoid intermediates via the Fritsch-Buttenberg-Wiechell rearrangement. This route provides a practical method for the formation of many polyyne species and offers a unique opportunity to explore the physical characteristics of conjugated polyynes. For example, X-ray crystallographic analysis of t-Bu end-capped polyynes shows a definitive experimental trend in reduced bond-length alternation, as has been predicted by numerous theoretical analyses.

In spite of significant efforts, the synthesis of polyynes longer than about 20 carbons has been difficult. Nevertheless, stable polyynes well beyond that of 10 contiguous acetylene units have now been achieved using an endgroup that is substantially larger than those previously explored, and a synthetic version of sp-hybridized carbon allotrope carbyne now seems within reach. This lecture will highlight recent advances in our synthesis of extended polyynes and carbyne, as well as interesting aspects of their physical and spectroscopic properties.