Oral presentation

Insights into the Bonding Nature of Arsenic, Phosphorus, and Sulphur Ylides: an answer from quantum crystallography

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Ylides are a class of chemical compounds classified as zwitterion by having a positively charged atom directly attached to a negatively charged atom. The most common types of ylides involve a positively charged heteroatom like nitrogen, phosphorus, sulphur, or arsenic attached to a negatively charged carbon atom (Figure 1(a)). [1,2] Ylides are textbook examples of the interplay between Lewis resonance forms and molecular reactivity/function. Phosphorus ylides or phosphonium ylides have been widely used in organometallic and organic synthesis, most famously as Wittig reagents in the Wittig reaction. Sulphur ylides (sulfonium ylides and sulfoxonium ylides) are also employed in organic synthesis, e.g. in the Johnson–Corey–Chaykovsky reaction. Another class of ylide compounds is arsenic ylides which are less commonly encountered compared to phosphor and sulphur ylides despite being discovered more than a century ago. However, arsenic ylides have been explored for their synthetic utility and attracted chemist's attention especially as a representative of a different synthesis mechanism compared to phosphorus ylides like Cyclopropanation reaction.

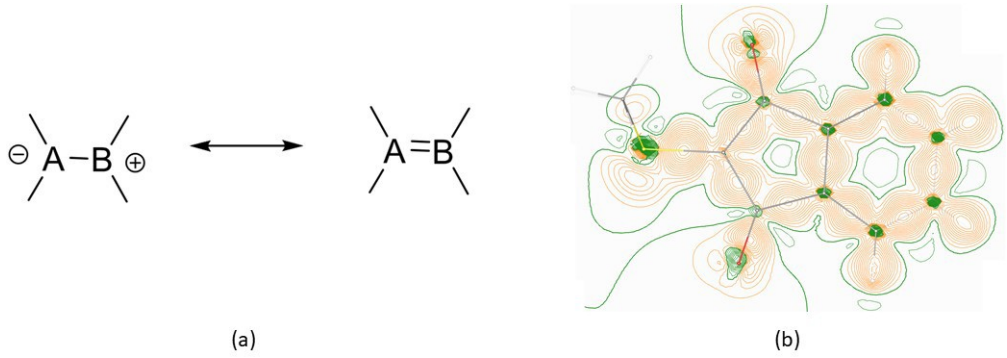

Figure 1. (a) Two resonance forms of an ylide compound, (b) 2-D deformation density map of sulphur ylide compound

In this regard, a combination of quantum crystallography (Hirshfeld atom refinement + x-ray constrained wave function fitting) and complementary bonding analysis [3] (QTAIM, ELI-D, EDA, NBO, VBT) reveals the nature and character of the P-C, S-C, and As-C bonds in ylides in detail. It is of practical importance and will also clarify concepts such as the hypervalency of P, S, and As atoms as well as the interplay between covalency and ionicity of heteroatom bonds. To the best of our knowledge, there are four experimental charge density studies about these bonds using multipole refinement, and there is no Hirshfeld atom refinement (HAR) and X-ray wavefunction (XCW) fitting study about these bonds. [4,5]

In this study, high-resolution XRD data is collected for one sulphur ylide, two phosphorus ylides, and two arsenic ylides. Then, X-ray wavefunction refinements (HAR + XCW fitting) plus complementary bonding analyses are performed to evaluate the ylide bonds. Our results demonstrate that the ylide bond is a charge-separated bond with a localized lone pair on the ylide carbon. This bond is an intermediate between covalent and ionic bond and the concept of double bond should be ruled out. Also, the theory of the hypervalent hetero atom (P, S, As) in ylides can be ruled out due to the minor contribution of d orbitals in the bonding and the low energy of this specific orbital interactions. From the energy perspective, the electrostatic term plays a significant role in stabilizing the bond and it influence the bonding more than orbital interactions.

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