Revisiting Kekulene: Synthesis and Single-Molecule Imaging

Iago Pozo[1], Zsolt Majzik[2], Niko Pavliček[2], Manuel Melle-Franco[3], Enrique Guitián[1], Diego Peña[1], Leo Gross[2], Dolores Pérez[1]

By the end of the 19th century, August Kekulé, inspired by a dream, was the first to understand the peculiar structure of benzene. Benzene, the smallest and archetypical aromatic compound, is a planar molecule which has a delocalized π electron cloud instead of discrete alternating single and double bonds. Kekulene is an artificial porous aromatic compound which shares the hexagonal shape of benzene yet it is made by joining together 12 benzene rings. It was first synthesized in 1978 and named after Kekulé to honour his achievements, Figure 1. In kekulene, as in other aromatic compounds, the way the π electrons populate the molecule results in particular molecular and electronic properties revealing their quantum chemical origin.

From benzene and kekulene to graphene, computer models are fundamental to understand and predict the properties of aromatic molecules and materials. Now, the applied computer modelling group lead by Manuel Melle-Franco at CICECO, a team of organic chemists from the University of Santiago de Compostela (Spain) and IBM Research Zurich (Switzerland) have proposed a new and simpler synthesis for kekulene. Besides, they have sublimated kekulene onto a metal surface and imaged it with ultra-high-resolution Atomic Force Microscopy (AFM), Figure 1.

The observation of single molecules of kekulene with exquisite detail backed-up by highly accurate computer models provides additional support for a molecular structure of kekulene, showing a clear and significant degree of bond localization, in accordance with the resonance structure predicted by the Clar model, Figure 2.

1 — Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) Universidade de Santiago de Compostela, (Spain)
2 — IBM Research–Zürich (Switzerland)
3 — Department of Chemistry & CICECO, University of Aveiro

FIGURE 1
Schematic synthesis of kekulene and constant-height AFM image with a CO-functionalized tip of kekulene on a copper surface.

FIGURE 2
Computed (a) versus experimental (b) molecular structure of kekulene. The colours grade with distance from 1.33 Å (red) to 1.40 Å (white) to 1.47 Å (blue). Bond lengths are in Å.