MS39 Crystallography at the nanoscale

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True molecular conformation and structure determination of remarkable polycyclic aromatic hydrocarbons

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Abstract

The true molecular conformation and the crystal structure of four large (30 – 46 C atoms) polycyclic aromatic hydrocarbons (PAHs)[1,2] were determined by direct methods from 3D electron diffraction (3D ED)[3] data, a result that could not be achieved by single crystal X-ray diffraction (XRD) due to limited crystal size and the thin leaflet morphology of the samples. Additionally, three of such compounds were isolated as by-products in the synthesis of similar materials and, therefore, were available only in very limited amount.

The main strength of 3D ED is the ability to perform single crystal diffraction on sub-micrometric areas. Therefore, this technique can be used for structure determination when crystal size is the limiting factor for single crystal XRD. Remarkably, this analytical protocol can be performed even on extremely small sample batches, which cannot be conveniently prepared for conventional powder XRD.

Moreover, the molecular conformation of two compounds could not be determined via classical spectroscopic methods due to the large size of the molecules and the occurrence of multiple and reciprocally connected aromatic rings. On the other hand, 3D ED data provided not only ab-initio structure solution, but also the unbiased determination of the internal molecular conformation. It is noteworthy that ab-initio crystal structure determination does not require information about the molecular conformation, but only a rough estimation of the atomic content of the unit cell.

The other two compounds were synthesised more than 50 years ago, but have hitherto remained structurally unsolved. All molecules have a considerable interest due to their optoelectronic properties, which led to the creation of a number of functionalised materials based on PAH backbones. Detailed synthetic routes, spectroscopic analyses and promising properties are also discussed.

References

1. Hall, C. L., Andrusenko, I., Potticary, J., Gao, S., Liu, X., Schmidt, W., Marom, N., Mugnaioli, E., Gemmi, M. & Hall, S. R. (2021) 3D Electron Diffraction Structure Determination of Terrylene, a Promising Candidate for Intermolecular Singlet Fission. ChemPhysChem 22(15), 1631-1637.

2. Andrusenko, I., Hall, C. L., Mugnaioli, E., Potticary, J., Schmidt, W., Gao, S., Marom, N., Hall, S. R. & Gemmi, M. (2022) True Molecular Conformation and Structure Determination by 3D Electron Diffraction of PAH By-Products Potentially Useful for Electronic Applications, in preparation.

3. Gemmi, M., Mugnaioli, E., Gorelik, T. E., Kolb, U., Palatinus, L., Boullay, P., Hovmöller, S. & Abrahams, J. P. (2019) 3D Electron Diffraction: The Nanoctystallography Revolution. ACS Cent. Sci. 5, 1315-1329.