#### **News & views**



#### Chemistry

# Carbon rings push limits of chemical theories

#### Przemysław Gaweł & Cina Foroutan-Nejad

Scientists are tantalized by the many forms that carbon could adopt – some of which are predicted to have extraordinary properties. The synthesis of three new all-carbon molecules is therefore a source of excitement. **See p.972 & p.977** 

Carbon has the ability to form a variety of covalent bonds, allowing it to adopt an extraordinary number of structural forms known as allotropes. Some of these, such as graphite and diamond, have been widely used for centuries. Others, including graphene, carbon nanotubes and fullerenes, have attracted attention over the past three decades because of their potentially revolutionary technological applications. In this issue, Gao *et al.*<sup>1</sup> (page 977) and Sun *et al.*<sup>2</sup> (page 972) report the synthesis and characterization of three new molecular forms of carbon. The findings shed fresh light on the much-debated properties and structures of all-carbon rings known as cyclocarbons.

Although many allotropes of carbon could

## California wildlife pays the cost of megafires

Wildfires are a natural part of forest life that help to shape diverse habitats. But the extreme 'megafires' that ravaged California in 2020 (pictured) and 2021 were more severe and about ten times more widespread than the yearly average in the region since records began, as Ayars et al. report in the Proceedings of the National Academy of Sciences (J. Ayars et al. Proc. Natl Acad. Sci. USA **120**, e2312909120; 2023).

To estimate the impact of these megafires on wildlife, the authors overlaid maps of burned areas and the predicted habitats of more than 500 mammals, reptiles, amphibians and birds. They found that 100 species had more than 10% of their habitat disturbed by fires, with up to 14% of their habitats being heavily burned. Although species that are of particular concern to conservationists were not estimated to be disproportionately affected, the actual impact on each species remains to be determined using data from post-fire surveys.

The authors warn that wildlife could struggle to adapt to increasingly severe megafires that are exacerbated by climate change, unless measures to restore natural, low-intensity wildfires are implemented with more urgency. Holly Smith

potentially be made (nearly 1,200 structures have been predicted from theoretical studies; see www.sacada.info), only a few have been isolated<sup>3</sup>. One group that has inspired scientists consists of two-coordinate materials, in which the carbon atoms bond to only two other carbon atoms; allotropes with threeor four-coordinate carbon atoms are more abundant. Two-coordinate forms of carbon include carbyne, which consists of long, linear chains of carbon atoms and is predicted to have exceptionally high tensile strength<sup>4</sup>, and cyclocarbons, which consist of rings of carbon atoms.

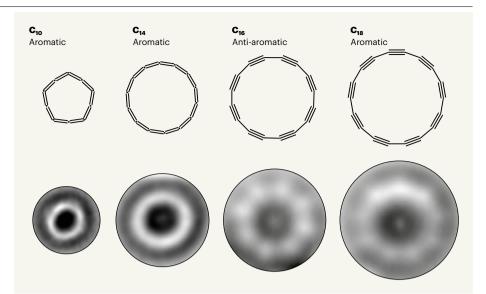
Because carbyne is unstable, the longrunning quest to synthesize it is fraught with difficulty – sometimes even leading to explosions<sup>5</sup>. But research aimed at making cyclocarbons has met with greater success. In the late 1980s, researchers set out to make cyclocarbons from molecular precursors. This work revealed the pivotal role of these compounds as intermediates in the synthesis of fullerenes<sup>6</sup>, but the cyclocarbons could be detected only in the gas phase. The limited success achieved in isolating cyclocarbons motivated theoreticians to investigate the molecular structures of these compounds using computational methods. This triggered an intense debate: depending on the theoretical method used, the predicted structures of some cyclocarbons were either polyynes (with alternating single and triple bonds) or cumulenes (consecutive double bonds; Fig. 1). Nevertheless, a general rule emerged: cumulenic structures are most abundant in the family of 'aromatic' cyclocarbons, whereas 'anti-aromatic' cyclocarbons are exclusively polyynic<sup>7</sup>.

The term 'aromatic'<sup>8</sup> in this context does not describe the odour of compounds, but instead is associated with stability. Aromatic molecules are generally stable, have equal distances between atoms in their rings and tend to preserve their highly symmetrical structures during chemical reactions. Antiaromatic molecules are less stable (and therefore much more reactive), have alternating long and short distances between atoms, and show lower symmetries in their structures.

Most aromatic and anti-aromatic molecules can be thought of as nanoloops of a conductive wire in which each carbon atom contributes one electron, which resides in an atomic orbital (known as a p orbital) perpendicular to the plane of the ring. In aromatic molecules, these electrons are delocalized around the molecular ring, whereas the corresponding electrons in anti-aromatic molecules tend to localize at particular positions, thereby producing the alternating bond distances. According to the Hückel rule of aromaticity, molecules with 4n + 2 electrons (where n is an integer) in their loop are aromatic, whereas those with 4n electrons are anti-aromatic.

When aromatic and anti-aromatic molecules are placed in a magnetic field, the loop electrons are induced to flow around them, just like a current in a superconductive wire. In aromatic molecules, the direction of the induced current follows a rule known as Lenz's law, whereas the current flows in the opposite direction in anti-aromatic molecules. The empirical correlation between stability, symmetry and current is assumed to be so robust that chemists often measure atomic distances, or calculate the induced current, to work out the stability (or instability) of molecules<sup>8</sup> – although the accuracy of this model is a persistent topic of debate.

Cyclocarbons can be thought of as nanoloops that contain two conductive wires, because each carbon shares two electrons with its neighbours. The electrons reside in two sets of *p* orbitals, which means that cyclocarbons can be double aromatic, or double anti-aromatic, molecules, or can produce a pair of electronic systems that have conflicting aromaticity. But how are the electrons distributed? Do equal numbers go into each nanoloop, or can a different number go into



**Figure 1** | **Experimentally determined structures of cyclocarbons.** The cyclocarbon family of molecules push the boundaries of a chemical phenomenon known as aromaticity, which affects compound stability: aromatic compounds are generally stable, whereas anti-aromatic compounds are unstable. The structures and chemical bonding in cyclocarbons are closely associated with aromaticity, but have been a topic of theoretical debate. The first cyclocarbon to be synthesized and characterized<sup>11</sup> was C<sub>18</sub>, which is aromatic and has a polyynic structure (consisting of alternating single and triple bonds). Three more cyclocarbons have now been prepared and characterized. Sun *et al.*<sup>2</sup> report that C<sub>10</sub> and C<sub>14</sub>, which are aromatic, have cumulenic structures (consisting of double bonds), whereas Gao *et al.*<sup>1</sup> find that C<sub>16</sub>, which is anti-aromatic, is polyynic. Scanning-probe microscopy images of each molecule are shown; the image for C<sub>18</sub> is from ref. 11.

each loop, thereby producing stable aromatic systems that conform to the (4n + 2) rule?

Hopes have been raised that the debate about cyclocarbon structures, which has run for decades, would be resolved by developments in scanning-probe microscopy (SPM) – a set of techniques in which a surface is imaged by scanning it with an atomically sharp tip. In 2009, an SPM technique was used to obtain an image of an aromatic molecule (pentacene) on a surface, with atomic resolution<sup>9</sup>. A separate thread of research has also shown that scanning tips can be used to manipulate atoms and

#### "The electrons in this C<sub>16</sub> molecule form two loops, each containing 16 electrons."

to induce chemical reactions on a surface<sup>10</sup>.

In the past few years, the threads of research into cyclocarbons and SPM have come together. In 2019, an aromatic cyclocarbon containing 18 carbon atoms (cyclo[18]carbon;  $C_{18}$ ) was made on a surface and characterized using the new SPM capabilities<sup>11</sup>. This showed that  $C_{18}$  is a polyyne, finally confirming its structure. However, this was only one cyclocarbon out of the several possible all-carbon rings that have been debated.

The preparation and structures of three new cyclocarbons, again using SPM techniques, have now been reported. Sun *et al.*<sup>2</sup> describe

 $C_{10}$  and  $C_{14}$ . They find that, unlike  $C_{18}$ , these aromatic cyclocarbons have cumulene structures. The authors' computations also suggest that the electronic current expected from the Lenz law can be magnetically induced in both molecules. By contrast, in independent work, Gao *et al.*<sup>1</sup> report that  $C_{16}$  has a polyynic structure. They find that the electrons in this molecule form two loops, each containing 16 electrons – which makes this the first experimental example of a double anti-aromatic cyclocarbon. As expected for anti-aromatic systems, the electronic current that can be induced in  $C_{16}$  flows in the opposite direction from that predicted by Lenz's law.

A curious fact about  $C_{16}$ , however, is that the molecule would be double aromatic if a pair of electrons moved from one set of p orbitals to the other set – that is, if there were 14 electrons in one loop and 18 in the other. Gao and colleagues' computations suggest that the hypothetical double aromatic  $C_{16}$  is higher in energy than the double anti-aromatic state, which is the ground state for this molecule. Such findings push the borders of the theory of aromaticity to their limits.

So, does molecular structure determine the aromaticity of a molecule, or does aromaticity define structure? The inherent multifaceted complexity of aromaticity means that a definitive answer to this question remains elusive. However, the characterizations of  $C_{10}$ ,  $C_{14}$  and  $C_{16}$  marks an important advance in the exploration of the sparsely populated 'chemical space' represented by cyclocarbons. The

### **From the archive**

A call to rename the proton in William Prout's honour, and an architect and sanitary engineer's treatise on how to keep a healthy house.

#### 100 years ago

The amazing advances in our knowledge of the composition and structure of matter achieved during the past few decades constitute an important ... step toward the establishment of the essential unity of the physical universe. In reviewing the epoch-making work of J. J. Thomson, whose electrical theory of matter underlies all recent developments in this field ... one should not be unmindful of the contribution made over a century ago by his compatriot, William Prout, an early apostle of unity. To all students of chemistry Prout's hypothesis, published in 1816, to the effect that all of the elements are formed from hydrogen by some process of condensation or grouping, has been familiar ... In recognition of the genius and insight of William Prout it is suggested herewith that the name "proton" recently assigned to the unit charge of positive electricity, be modified, with some small sacrifice of etymological accuracy, to "prouton".

From Nature 1 December 1923

#### 150 years ago

What a House should be, versus Death in the House. By William Bardwell, Architect and Sanitary Engineer - The subject of drainage ... has been forced into prominence by the dangerous illness of the Prince of Wales, in the Autumn of 1871: and this work meets to some extent the demand for further and better information on the subject ... It would be interesting to have had some references given to sanction our author in claiming the authority of the Duke of Wellington, together with that of ... his successors, for the practice of placing their beds nearly north and south so as to be in the line of the magnetic current. The theory no doubt has its advocates, but can hardly be of universal application, as there are many sound sleepers at all degrees of orientation.

From Nature 27 November 1873



compounds provide new data points, which are poised to enhance theoretical models and deepen our comprehension of aromaticity's role in molecular architecture.

#### Przemysław Gaweł and Cina Foroutan-Nejad

are at the Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland.

e-mails: przemyslaw.gawel@icho.edu.pl; cina.foroutan-nejad@icho.edu.pl

- 1. Gao, Y. et al. Nature 623, 977–981 (2023).
- 2. Sun, L. et al. Nature 623, 972-976 (2023).

#### **Climate change**

- Hoffmann, R., Kabanov, A. A., Golov, A. A. & Proserpio, D. M. Angew. Chem. Int. Edn 55, 10962–10976 (2016).
- Itzhaki, L., Altus, E., Basch, H. & Hoz, S. Angew. Chem. Int. Edn 44, 7432–7435 (2005).
- 5. Baughman, R. H. Science 312, 1009-1110 (2006).
- McElvany, S. W., Ross, M. M., Goroff, N. S. & Diederich, F. Science 259, 1594–1596 (1993).
  - Anderson, H. L., Patrick, C. W., Scriven, L. M. & Woltering, S. L. Bull. Chem. Soc. Jpn 94, 798–811 (2021).
  - Merino, G. et al. Chem. Sci. 14, 5569–5576 (2023).
    Gross, L., Mohn, F., Moll, N., Liljeroth, P. & Meyer, G.
  - Science **325**, 110–1114 (2009).
  - Hla, S.-W., Bartels, L., Meyer, G. & Rieder, K.-H. Phys. Rev. Lett. 85, 2777–2780 (2000).
  - 11. Kaiser, K. et al. Science **365**, 1299–1301 (2019).

The authors declare no competing interests.

# Tackling poverty need not impede climate action

#### Katharine L. Ricke & Gordon C. McCord

A study has revealed that eliminating extreme poverty would result in a relatively small increase in global greenhouse-gas emissions, dispelling the idea that efforts to combat climate change and poverty are incompatible. **See p.982** 

Among the 17 goals set out in the United Nations' 2030 Agenda for Sustainable Development (see sdgs.un.org/goals), eliminating poverty tops the list, and the 13th goal - combating global climate change - puts the 2030 agenda alongside the 2015 Paris climate agreement in terms of its impact on international climate policymaking<sup>1</sup>. But how does stamping out poverty affect the bid to stop climate change? Not as much as one might think, it turns out. On page 982, Wollburg et al.<sup>2</sup> estimate that eliminating extreme poverty by 2050 would raise annual global greenhouse-gas emissions by less than 5%. And this number shrinks by a factor of ten with a climate-smart version of growth that includes improved technologies and reduced inequality.

The authors analysed a rich data set<sup>3</sup> containing the income distributions of 168 countries, drawn from household surveys that were compiled by the World Bank, with which Wollburg and colleagues are affiliated. They looked at the relationships between income and consumption, and estimated future changes to a country's economy on the basis of information about its past and that of other countries. The authors then extrapolated past trends to calculate the amount of economic growth needed to reduce extreme poverty levels in all countries to 3%, the threshold below which the World Bank considers extreme poverty eliminated. The authors conducted similar analyses of the relationships between income and energy use, as well as energy use and

greenhouse-gas emissions, to estimate how much this economic growth would increase the atmospheric concentrations of gases linked to global warming.

The main driver of poverty reduction is the growth of a country's overall economy<sup>4</sup> - the remainder can be linked to reductions in income inequality. The assumption is that this growth will have an impact on the climate, because increased production and incomes give rise to elevated emissions<sup>5</sup>. Previous studies<sup>6-8</sup> have estimated the rise in emissions associated with increasing the consumption of only impoverished populations, and reported numbers ranging from less than 1% to 3% of contemporary global emissions. However, Wollburg et al. assumed that eliminating poverty would increase the consumption of a country's entire population, not just those who are living in poverty. Intuitively, it could be expected that this way of calculating would greatly increase the estimated impact of eradicating poverty on climate change. But that is not what the authors found.

Even when Wollburg *et al.* applied conservative assumptions of no energy technology or efficiency improvements beyond those observed in other countries in the past, they found that eliminating extreme poverty would increase annual global emissions in 2050 by just 4.9% of their 2019 value (Fig. 1). When modest reductions in income inequality, increases in energy efficiency and improvements in energy technology are included in