

Covalent bonds share electron pairs between two atoms and make up the skeletons of most organic compounds in single, double and triple bonds. Meanwhile, Pauling proposed a concept of covalent bonds with one unpaired electron ('one-electron σ -bonds') in 1931, which is shared between two atoms. In striking contrast to the large body of work on electron-pair bonds, the paucity of examples with one-electron bonds is remarkable, which is most likely due to their intrinsic weakness. So far, merely five compounds have reported on the subject of one-electron bonds between atoms other than carbon [P•P (*Science* **1998**, 279, 2080), Cu•B (*JACS* **2013**, 135, 3792), B•B (*ACIE* **2014**, 53, 4832), and Sn•Sn (*JACS* **2024**, 146, 2333)]. Importantly, since Pauling's postulation almost a century ago, direct evidence (*e.g.*, X-ray structural analysis) that would corroborate the presence of such one-electron bonds between carbon atoms, which is arguably the most prevalent element in organic chemistry, has remained recalcitrantly elusive. Although several attempts have been made to directly prove the presence of a one-electron bond, in almost all cases these one-electron bonded species were only detected transiently using methods such as electron-spin-resonance spectroscopy [*cf.* *e.g.*, *JACS* **1981**], which constitutes circumstantial rather than direct evidence. Accordingly, consensus in the chemistry community had been up until now that compounds with such a weak bond are not isolable.

$R_3C\bullet CR_3^+$ radical cations are promising models with which to investigate C•C one-electron σ -bonds, and stabilizing such compounds is as important a task as it is challenging. One approach to circumvent this obstacle is to use hexaphenylethane (HPE) derivatives, which can be expected to provide a suitable framework because their oxidation would lead to the formation of triarylmethyl cation and triarylmethyl radical units, which are well known, relatively stable, carbocations and radicals.

In this article, the candidate's group reports the isolation of a compound with a one-electron σ -bond between carbon atoms by means of the one-electron oxidation of a HPE-type hydrocarbon with an elongated C–C single bond [*Chem* **2018**, 4, 795, *Nature* **2024**, 634, 347]. The presence of the C•C one-electron σ -bond (2.921(3) Å at 100 K) was confirmed experimentally by single-crystal X-ray diffraction analysis and Raman spectroscopy for the single crystals of the obtained salt, and theoretically by density functional theory calculations. The salts can be stored under ambient conditions for at least two weeks without appreciable decomposition, and remained intact even during high-temperature X-ray measurements at 400 K.

This incredibly stable C•C one-electron bond is furthermore characterized by a near-infrared (NIR) absorption that can be attributed to the small energy splitting between the σ and σ^* orbitals, which is another evidence of the presence of the bond. Thus, in contrast to common organic NIR-absorbing materials, which are typically employed for bio-imaging and generally require a large π -skeleton, the C•C one-electron bond can activate NIR-absorbing properties even with just one bond.

This discovery, made almost 100 years after Pauling's initial postulation, can be expected to deepen further understanding of bonding theory, and holds promise for the future development of a new class of functional materials.