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Direct evidence for a carbon–carbon one-electron σ -bond

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Summary:

Covalent bonds, one of the most basic types of chemical bonds, serve as the skeletal framework in most organic compounds. Since Lewis's formulation 100 years ago¹, the fundamental principles of covalent bonds have been widely accepted. Yet, in contrast to the large body of electron-pair bonds, e.g., single, double, and triple bonds, examples of one-electron bonds remain scarce, most likely due to their intrinsic weakness^{2–5}. Although several pioneering studies have reported one-electron bonds between heteroatoms, direct evidence for one-electron bonds between carbon atoms, the most ubiquitous element in organic chemistry, still remains elusive. Here, we report the isolation of a compound with a one-electron σ -bond between carbon atoms via the one-electron oxidation of a hydrocarbon with an elongated C–C single bond^{6,7}. The presence of the C•C one-electron σ -bond [2.921(3) Å at 100 K] was experimentally confirmed by single-crystal X-ray diffraction analysis and Raman spectroscopy, and theoretically confirmed by DFT calculations. The results of this paper unequivocally demonstrate the existence of a C•C one-electron σ -bond, which was postulated nearly a century ago, and can thus be expected to pave the way for further development in this area of chemistry.

Main Text:

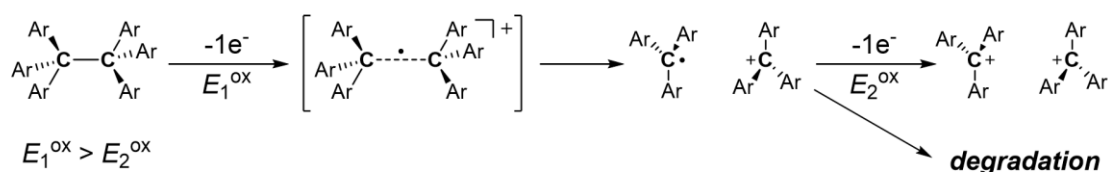
Covalent bonds, in which an electron pair is shared between two atoms, are ubiquitous in organic chemistry for the construction of an abundance of molecular skeletons. Accordingly, unveiling the nature of covalent bonds is of special importance to gain a deeper understanding of chemical phenomena. The concept of two atoms sharing an electron pair, which was initially proposed by Lewis in 1916¹ and then termed “covalent bond” in 1919 by Langmuir⁸, remains crucial to understanding chemical bonding.

Subsequently, Pauling proposed a concept of covalent bonds with one unpaired electron ('one-electron σ -bonds'), which is shared between two atoms⁹. In 1931, Pauling postulated the existence of one-electron σ -bonds using the $\text{H}_2^{\bullet+}$ radical cation as a simple model. Such one-electron σ -bonds are expected to be much weaker than typical two-electron σ -bonds, and therefore, their properties have been primarily investigated theoretically^{10–13}. Nevertheless, few studies on *in-situ*-generated radical anions^{14–17} such as $\text{R}_3\text{B}^{\bullet}\text{BR}_3^-$ and radical cations^{10,18–20} such as $\text{R}_3\text{E}^{\bullet}\text{ER}_3^+$ (E = C, Si, and Ge) based on electron-spin-resonance (ESR) measurements have been reported. Other reports have described the spectroscopic identification of chemical species with one-electron σ -bonds that were generated as single components; however, these compounds have not been isolated^{21,22}. The number of X-ray crystallographic studies on

species that contain one-electron σ -bonds is particularly scarce, i.e., they are limited to P•P, B•B, and Cu•M (M = B, Al and Ga) bonds^{2–5}. It is important to note here that although species with C•C one-electron σ -bonds have been proposed as intermediates in chemical reactions such as the Cope rearrangement, there is no experimental evidence by e.g., X-ray crystallography for one-electron σ -bonds between carbon atoms^{23–28}. Yet, elucidating the nature of one-electron σ -bonds between two carbon atoms is essential to gain a deeper understanding of chemical-bonding theories and would provide further insights into chemical reactions.

Here, we present the first comprehensive investigation of a compound that contains a one-electron σ -bond between two carbon atoms, which was obtained from the one-electron oxidation of a hydrocarbon that features an extremely elongated C–C single bond. The presence and characteristics of the C•C one-electron σ -bond were demonstrated experimentally via single-crystal X-ray diffraction analysis and Raman spectroscopy and supported theoretically by DFT calculations.

Typical oxidation processes in HPEs



Oxidation in the HPE derivative with an ultralong C–C single bond

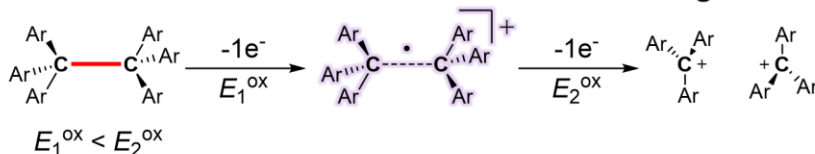


Fig. 1. Proposed redox mechanisms in hexaphenylethane (HPE) derivatives

Synthesis and characterization of $1^{+\bullet}$

$R_3C\cdot CR_3^+$ radical cations are promising models to investigate C•C one-electron σ -bonds^{18,20}. However, reports on molecules that contain a C•C one-electron σ -bond currently remain elusive due to their intrinsically high reactivity, 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.

An important issue in this context is that most redox-active HPEs undergo a process close to a one-step two-electron oxidation to produce two triarylmethyl cations because the oxidation potential for the bond-dissociated radical, which is readily generated by the C–C bond scission of the radical cation intermediate, is much less positive than that for neutral σ -bonded species ($E_1^{ox} > E_2^{ox}$) (Fig. 1, top). To obtain a radical cation with a C•C one-electron σ -bond, the oxidation of HPEs must proceed in a stepwise manner, i.e., the level of the highest occupied molecular orbital (HOMO) for the neutral state must be higher than that of the singly occupied molecular orbital (SOMO) for the radical cation ($E_1^{ox} < E_2^{ox}$). Although raising the HOMO level is considered to be essential, the introduction of electron-donating heteroatoms into HPEs is not effective because it simultaneously raises the HOMO level of the neutral species and the SOMO level of the radical cations. Thus, alternative approaches for achieving a stepwise oxidation process are required.

We tackled this issue by focusing on another notable feature of HPEs, i.e., the central C–C single bond is elongated beyond 1.6 Å due to the steric hindrance imposed by the aryl groups surrounding the bond^{29–33}. This bond elongation causes an increase in the HOMO level via a through-bond interaction between the elongated C–C bond and the aryl groups. Thus, the bond elongation in HPEs provides an optimal approach to realize an energy reversal between the HOMO of the neutral state and the SOMO of the radical-cation state without relying on the introduction of electron-donating heteroatoms (Fig. 1, bottom).

HPE **1**^{6,7} bears two spiro-dibenzocycloheptatriene (DBCHT) units and thus satisfies the aforementioned key factors, i.e., it has an extremely elongated Csp^3 – Csp^3 single bond (1.806(2) Å at 400 K), which is the greatest value among hitherto reported HPEs. Such an extremely elongated C–C bond increases the HOMO level via a through-bond interaction, resulting in a stepwise oxidation process [$E_p^{ox1} = +0.57$ V and $E_p^{ox2} = +0.69$ V vs SCE] that was observed by cyclic voltammetry³⁴. Furthermore, the rigid acenaphthylene core causes not only a bond elongation in the neutral state but also provides the precise C···C distance required to form a one-electron bond. The naphthalene core, on the other hand, is not suitable to cause the stepwise oxidation in the corresponding hydrocarbon, even though that worked well in the case of the B•B one-electron bond reported by Gabbaï *et al.*²¹. We envisaged that HPE **1** could potentially serve as a suitable platform to stabilize the C•C one-electron σ -bond via an intramolecular core–shell strategy.

Fig. 2a shows the redox reactions of **1**. A two-electron oxidation was achieved by treating **1** with iodine (3.0 eq.) to furnish dication salt $1^{2+}(I_3^-)_2$, single crystals of which were obtained after recrystallization from CH_2Cl_2/Et_2O . Meanwhile, the one-electron oxidation of **1** with iodine (1.5 eq.) provided $1^{+\bullet}I_3^-$ as a dark brown solid that is sparingly soluble in organic solvents such as CH_2Cl_2 and MeCN. The formation of paramagnetic species was confirmed by the absence of any 1H NMR signals and the presence of a characteristic doublet ESR signal in solution. Recrystallization of the radical cation salt $1^{+\bullet}I_3^-$ from MeCN/ Et_2O afforded dark violet single crystals suitable for X-ray diffraction measurements. Upon reduction of the cationic

species with zinc powder, the original compound **1** was restored.

X-ray analysis

The obtained single crystals were subjected to an X-ray diffraction analysis in order to elucidate the redox-state-dependent differences in the molecular structures. The X-ray structure of dication $\mathbf{1}^{2+}$ in $\mathbf{1}^{2+}(\text{I}_3^-)_2$ exhibits a twisted conformation with a twisting C1–C3–C4–C2 angle (θ) of $20.8(6)^\circ$, while both DBCHT moieties are planar (Fig. 2c). As in the case of $\mathbf{1}^{2+}(\text{I}_3^-)_2$, typical dibenzocycloheptatrienylium (cation) and dibenzocycloheptatrienyl (radical) derivatives would be expected to exhibit a preference for planarity, which is more conducive to π -stacking and electron delocalization^{35–37}. In contrast, an eclipsed conformation with a small θ value of $2.19(19)^\circ$ was observed in the X-ray structure of $\mathbf{1}^{+\bullet}$ in $\mathbf{1}^{+\bullet}\text{I}_3^-$ (Fig. 2d, e). One of the DBCHT moieties in $\mathbf{1}^{+\bullet}$, i.e., the one containing C1, adopts a bent geometry with larger dihedral angles between the a-e planes (Fig. 2). The concave surface of the bent seven-membered ring faces the other DBCHT unit, i.e., the one containing C2, which exhibits an almost planar geometry. The estimated standard deviation of the structural parameters (bond length: 0.004 Å; bond angle: 0.3 °) and R indices ($R1 = 0.0220$; $wR2 = 0.0569$) for $\mathbf{1}^{+\bullet}\text{I}_3^-$ were sufficiently small to confirm the unsymmetrical bent-planar structure, and the nearly perfect round shape of the thermal ellipsoids of C1 and C2 excludes the possibility of a disordering copresence of **1** or $\mathbf{1}^{2+}$ at the site of $\mathbf{1}^{+\bullet}$. Crystals of $\mathbf{1}^{+\bullet}\text{I}_3^-$ 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 (Fig. S4). The observed geometrical difference between $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{2+}$ is intrinsic and reproducible, which was confirmed by analyzing multiple single crystals of $\mathbf{1}^{+\bullet}\text{I}_3^-$ and $\mathbf{1}^{2+}(\text{I}_3^-)_2$.

This distinctive geometry deviates from the typical planar conformation of a pimer composed of cationic and radical moieties/molecules^{38–40}. Interestingly, contrary to the unsymmetric structure of $\mathbf{1}^{+\bullet}\text{I}_3^-$, the bond lengths within the two different DBCHT moieties are almost identical (Tables S1, S2), which suggests that the spin and positive charge are delocalized over the two DBCHT moieties in $\mathbf{1}^{+\bullet}\text{I}_3^-$, i.e., spin and charge-separated states are not favored. Other effects between the two DBCHT moieties stem most likely from the stabilization of the unique and unsymmetric bent conformation. At present, we hypothesize that the molecular structure of $\mathbf{1}^{+\bullet}$ with an unsymmetric bent-planar geometry is similar to that of **1**, which implies an inheritance from the covalent-bond nature between the C1 and C2 atoms. In fact, the short contact between the C1 and C2 atoms ($2.921(3)$ Å at 100 K) was confirmed in the X-ray structure of $\mathbf{1}^{+\bullet}\text{I}_3^-$ (Fig. 2e). The sum of the three bond angles around the C1 (359.3°) and C2 (359.6°) atoms indicates that each atom is sp^2 hybridized despite the unsymmetrical bent-planar geometry. This finding is consistent with previous examples of weak C $\cdots$ C bondings, in which the carbon atoms involved exhibit a preference for sp^2 hybridization^{41,42}. Focusing on the intramolecular C $\cdots$ C distance between the two DBCHT units, although some interatomic distances (2.92 – 3.32 Å) closer to the naphthalene skeleton were found to be less than the sum of the van der Waals radii of carbon atoms (3.40 Å), most are greater (3.44 – 3.79 Å), indicating an unfavorable conformation for stabilization by π - π interactions (Fig. S10, Table S1). This behavior contrasts with the usual planar π -systems, suggesting that stabilizing interactions other than π - π stacking are occurring between the DBCHT units. In the crystal, short intermolecular contacts between one DBCHT unit and I_3^- (~ 3.5 Å; sum of the van der Waals radii: 3.8 Å) were observed. However, they correspond to the proximity of the σ -hole, a positively polarized site, in the I_3^- ion and the cationic π -surface of DBCHT, and accordingly, this intermolecular interaction has little effect on the geometrical features of $\mathbf{1}^{+\bullet}$ in crystal. It is also worth noting here that residual electron density between the C1 and C2 atoms is present in the Fo–Fc map that was obtained from the X-ray analysis of $\mathbf{1}^{+\bullet}\text{I}_3^-$ (Fig. 3a–c), which proves electron sharing between the C1 and C2 atoms. This electron sharing contributes to the

molecular stability, which predestines radical cation $\mathbf{1}^{\bullet+}$ to serve as a host for a C•C one-electron σ -bond with a bond length of 2.921(3) Å. In the case of the B•B one-electron bond, which is based on the naphthalene core, a similar interatomic distance was predicted²¹, while a smaller value was determined in the corresponding molecule with a biphenyl core. This difference should most likely be interpreted in terms of the rigidity of the π -framework.

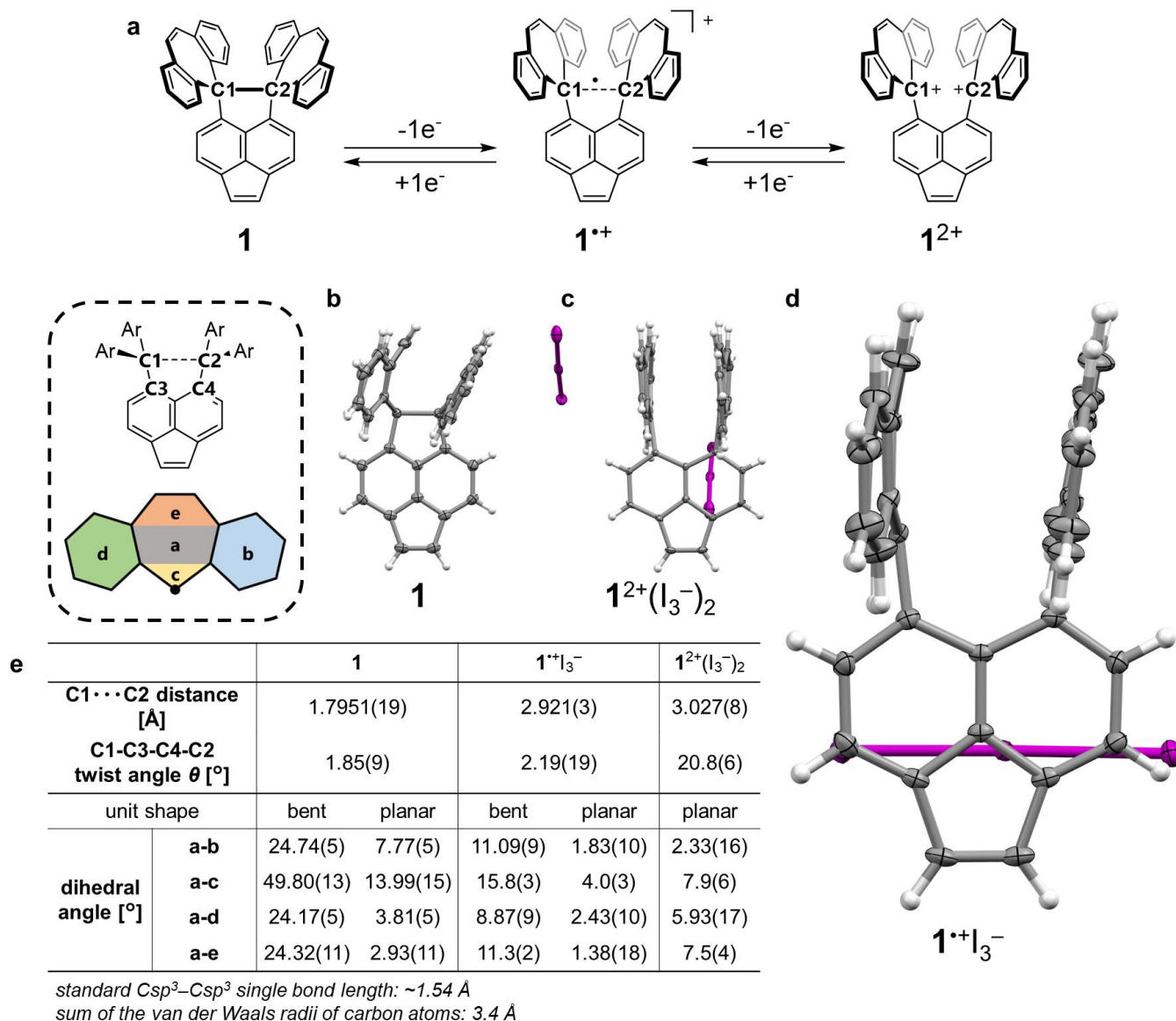


Fig. 2. Redox reactions and X-ray structures. **a**, Redox interconversion of **1**. X-ray structures of **(b)** **1** and **(d)** $\mathbf{1}^{\bullet+}\text{I}_3^-$ at 100 K and **(c)** $\mathbf{1}^{2+}(\text{I}_3^-)_2$ at 110 K with thermal ellipsoids at 50% probability. **e**, Structural parameters determined at 100 K for **1** and $\mathbf{1}^{2+}(\text{I}_3^-)_2$ and at 110 K for $\mathbf{1}^{\bullet+}\text{I}_3^-$. Due to the phase transition occurring at ~100 K, the X-ray analysis of $\mathbf{1}^{2+}(\text{I}_3^-)_2$ was conducted at 110 K; disordered I_3^- is omitted for clarity in $\mathbf{1}^{2+}(\text{I}_3^-)_2$.

Experimental and theoretical analyses

To verify whether this electron sharing corresponds to the bond, a single crystal of $1^{+}I_3^{-}$ was subjected to Raman spectroscopy at 298 K in order to obtain direct information regarding the force constant of the bond. The experimentally obtained and simulated Raman spectra of 1^{+} are shown in Fig. 3d, e. The simulated spectrum obtained from DFT calculations at the UM06-2X/6-311+G** level accurately reproduced the experimental results. The observed Raman shift ($1^{+}I_3^{-}$: 379 cm^{-1}) attributed to the symmetric C1–C2 stretching vibration is significantly lower than that for neutral 1, which contains an ultralong C–C single bond (589 cm^{-1})^{6,7}. However, this Raman shift is higher than that observed in molecules that contain C⋯C bonding interactions beyond 2.0 Å ^{41,42}. This contrasts with the common absence of Raman shifts for weak interactions in π -stacked molecules such as pimers.

Next, DFT calculations were carried out in order to elucidate additional information on the strength of the C•C one-electron σ -bond. The estimated force constant for 1^{+} (56.8 N m^{-1}), which was obtained as a second derivative of the energy with respect to the bond length at the (U)M06-2X/6-31+G** level based on the Lennard–Jones potential, is much smaller than that for **1** (113.7 N m^{-1}) or ethane (445.9 N m^{-1}). The estimated force constant is in good agreement with the calculated value (50.8 N m^{-1}) obtained from the relationship between the force constant and the vibrational frequency using the value of the observed Raman shift of the symmetric C1–C2 stretching vibration (for details, see the Supplementary Information). These results suggest a covalent nature of the electron sharing between the C1 and C2 atoms in $1^{+}I_3^{-}$.

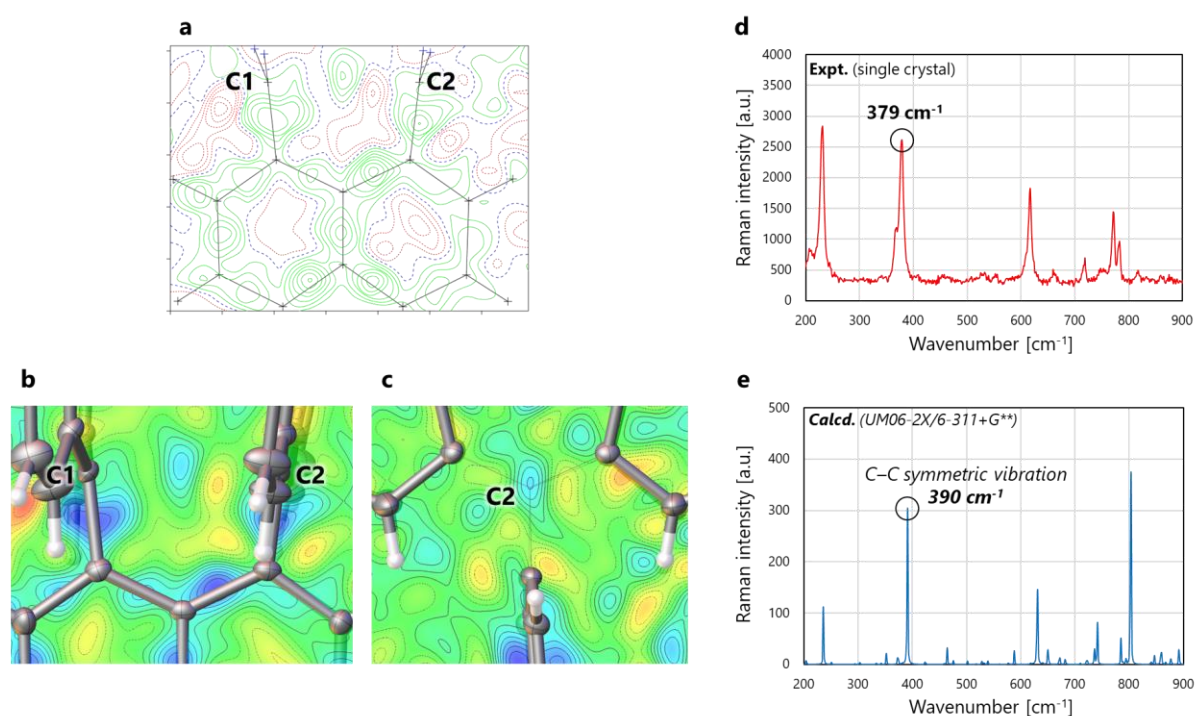


Fig. 3. Experimental evidence of the presence of a C•C one-electron σ -bond in $1^{+}(I_3^{-})$.

Experimentally obtained Fo–Fc maps of $1^{+}I_3^{-}$ at 100 K (**a** and **b**) on the C1–C3–C4–C2 plane and (**c**) on its orthogonal plane through the midpoint between the C1 and C2 atoms (C2→C1 direction). Residual electron density is shown in green (**a**) and blue (**b** and **c**). **d**, Raman spectrum measured at 298 K using a single crystal of $1^{+}I_3^{-}$. **e**, Simulated Raman spectrum for 1^{+} obtained from DFT calculations at the UM06-2X/6-311+G** level.

Le Floch *et al.* have reported that the radical anion of the calixarene exhibits a short C $\cdots$ C distance (3.323(3) Å)⁴³. From a theoretical point of view, the coefficients of the SOMO indicate that a bonding orbital between the carbon atoms in close proximity was not formed since they reside on the nodal plane. Thus, a detailed investigation is needed to verify whether this short contact represents a bond or is merely due to physical proximity. To gain further insight into the electronic structure, DFT calculations for **1**^{•+} were performed at the UM06-2X/6-311+G** level based on the X-ray coordinates. The results indicate that the SOMO, the lowest unoccupied molecular orbital (LUMO), and the spin density are mainly located on the C1 and C2 atoms (Fig. 4a, b, c). According to the shape of the orbitals, the SOMO and LUMO of **1**^{•+} represent the σ -type bonding and σ^* -type antibonding orbitals, respectively. In the natural bond orbital analysis of **1**^{•+}, both orbitals were confirmed for the C1 and C2 atoms as well. The C1–C2 bond exhibits 0.3–0.4% 2s character and 99.6–99.7% 2p character, with 0.76 electrons involved in the bond. Equal values of a positive charge for both C1 (0.05) and C2 (0.05) atoms in **1**^{•+} were estimated using natural population analysis (NPA) methods, indicating a delocalized charge distribution within the DBCHT moieties. The NPA analysis also predicted a relatively large spin-density distribution on the C1 (0.26) and C2 (0.24) atoms. A localized molecular orbital (LMO) analysis using the Foster-Boys method revealed that the contribution of the C1 (28.0%) and C2 (27.5%) atoms in the α -SOMO is dominant and that the contributions of the other atoms is <5%. The shape of the localized α -SOMO clearly reflects the formation of the σ -orbital (Fig. S21). Considering these results and the comparable bond lengths in each DBCHT moiety, the contribution of a coordinating-type bonding interaction can be excluded, i.e., these results suggest that a σ -bond between carbon atoms could be maintained even if less than one electron is involved. Furthermore, we carried out bond topological analyses including quantum theory of atom in molecules (QTAIM) and electron localized functions (ELF) for the whole series. Each parameter for **1**^{•+} exhibits an intermediate value between those of bonded **1** and non-bonded **1**²⁺, which suggests that **1**^{•+} possesses an intermediary nature. This finding is consistent with the notion of the presence of a one-electron bond, which would be expected to fall between a two-electron bond and a non-bonded state.

In their entirety, the experimental and theoretical results indicate that the short C1 $\cdots$ C2 contact with a value of 2.921(3) Å in **1**^{•+}I₃[−] is, while weak, the first example of a C•C one-electron σ -bond.

To investigate the properties of the compound from the photochemical point of view, we recorded the UV/Vis/near-infrared (NIR) spectrum of **1**^{•+}I₃[−] in CH₂Cl₂. An NIR absorption band was observed at ~2000 nm ($\lambda_{\text{max}} \approx 1405$ nm) (Fig. 4d, e), which cannot be explained by disproportionation ($2 \times \mathbf{1}^{\bullet+} \rightleftharpoons \mathbf{1} + \mathbf{1}^{2+}$) because neither **1** nor **1**²⁺ exhibits such an NIR absorption (Figs. 4h, i and S15). In solution, **1**^{•+} could exist in an equilibrium between the σ -bonded form and the pimer-like form predicted by DFT calculations (for details, see the Supplementary Information). To confirm that the pimer-like form is not responsible for the NIR absorption, a solid-state absorption spectrum was recorded using a single crystal of **1**^{•+}I₃[−], which showed an NIR absorption in the same region as that in solution (Fig. 4f, g). Thus, the NIR absorption for **1**^{•+}I₃[−] can be attributed to the σ – σ^* transition of the weak C•C one-electron bond.

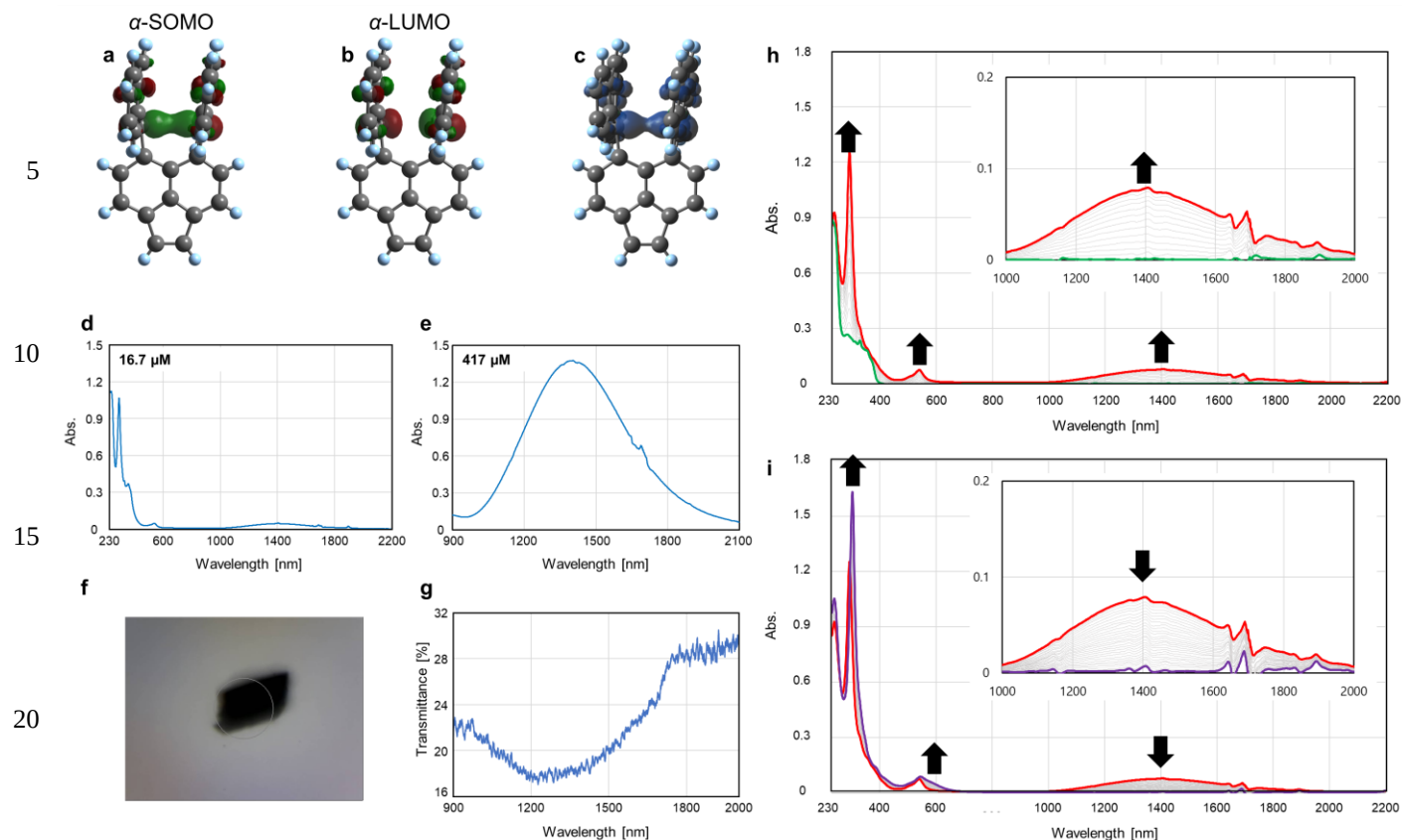


Fig. 4. Electronic properties of $1^{\bullet+}$ with a C•C one-electron σ -bond. Kohn–Sham orbitals of the (a) α -SOMO and the (b) α -LUMO (isovalue = 0.05), (c) spin density (isovalue = 0.004) obtained from DFT calculations at the UM06-2X/6-311+G** level. The atomic coordinates of the X-ray structure of $1^{\bullet+}I_3^-$ at 100 K were used for the calculations. UV/Vis/NIR absorption spectra (d and e) in CH_2Cl_2 and (g) for a single crystal of $1^{\bullet+}I_3^-$. f, Photograph of a single crystal of $1^{\bullet+}I_3^-$. Changes in the UV/Vis/NIR spectra upon constant-current electrochemical oxidation of **1** (11.1 μ M, 30 μ A, every 2 min) in CH_2Cl_2 containing 0.05 M Bu_4NBF_4 as a supporting electrolyte. h, First step (0–28 min, **1** to $1^{\bullet+}$); i, Second step (28–90 min, $1^{\bullet+}$ to 1^{2+}).

Conclusion

HPE derivative **1**, which contains an extremely elongated Csp^3-Csp^3 single bond due to the through-bond interactions between the aryl groups, was subjected to a stepwise oxidation process. After one-electron oxidation of **1** with iodine, the radical cation salt $\mathbf{1}^{\bullet+}I_3^-$ was isolated as a stable entity. The unusual proximity of the C1 and C2 atoms (2.921(3) Å at 100 K) in $\mathbf{1}^{\bullet+}I_3^-$ can be rationalized in terms of the formation of a C•C one-electron σ -bond. The presence of a C•C one-electron σ -bond was experimentally confirmed by observing electron sharing between the C1 and C2 atoms in the Fo–Fc maps obtained from the single-crystal X-ray diffraction analysis and by the Raman shift attributed to the C1–C2 symmetric vibration. The analysis of the experimentally obtained X-ray structure in combination with a thorough theoretical investigation revealed that the present C•C one-electron σ -bond consists of p orbitals of sp^2 carbon atoms. As a result of the formation of the incredibly stable C•C one-electron bond, NIR absorption was observed owing to the small energy splitting between the σ and σ^* orbitals. These results thus constitute the first piece of experimental evidence for a C•C one-electron σ -bond, which can be expected to pave the way for further developments of the chemistry of this scarcely explored type of bonding with stimulating the theoretical interest in evaluating the boundary between the bonded and non-bonded states.

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Methods

General information

All commercially available compounds were used without further purification unless otherwise indicated. MeCN was dried prior to use by distillation from CaH₂. Column chromatography was performed on silica gel (Wakogel[®] 60N; neutral; particle size: 38-100 μm). ¹H and ¹³C NMR spectra were recorded on a BRUKER AscendTM 400 (¹H/400 MHz and ¹³C/100 MHz) spectrometer. Mass spectra were recorded on a JEOL JMS-T100GCV spectrometer in FD mode (GC-MS&NMR Laboratory, Research Faculty of Agriculture, Hokkaido University). Melting points were measured on a Stanford Research Systems MPA100 Optimelt for powder samples and on a YANACO MP-J3 for single crystals; all values are uncorrected. The Raman spectroscopy using a 785 nm laser was carried out on a RENISHAW inVia Reflex at the OPEN FACILITY, Hokkaido University Sousei Hall. IR spectra were measured on a Shimadzu IRAffinity-1S spectrophotometer (attenuated total reflection (ATR) mode) for powder samples and on a JASCO IRT-5200FT/IR-6600 spectrophotometer for single crystals (Transmission Mode). X-band CW-EPR measurements were conducted using a Bruker BioSpin EMX Plus. Solid-state UV/Vis/NIR spectra were measured on a microscopic spectrometer (MSV 5200, JASCO; Transmittance Mode), while solution-state UV/Vis/NIR spectra were recorded on a JASCO V-770 spectrophotometer.

DFT calculations were performed using the Gaussian 16W⁴⁴ program package. Parts of the DFT calculations for **1**^{•+} were performed with the atomic coordinates obtained from the X-ray diffraction analysis of sample 1 of **1**^{•+}I₃⁻ at 100 K. Version 3.8 of the Multiwfn software⁴⁵ was used for LMO (Foster-Boys method) and topological analysis (QTAIM and ELF) of the electron density that was obtained from the DFT calculations. The NBO analyses were performed using Version 3.1 of the NBO⁴⁶ function within the Gaussian 16W program package.

A suitable crystal was selected and used for the measurement on a Rigaku XtaLAB Synergy (Cu-Kα radiation, λ = 1.54184 Å) with HyPix diffractometer. Using Olex2⁴⁷, the structure was solved with the SHELXT⁴⁸ structure solution program using Intrinsic Phasing and refined with the SHELXL⁴⁹ refinement package using Least Squares minimization.

Starting material

HPE **1** was prepared according to literature procedures⁶.

Synthesis of radical cation salt **1^{•+}I₃⁻.** **1** (4.74 mg, 8.93 μmol) was added to a solution of iodine (1.70 mg, 13.4 μmol) in dry CH₂Cl₂ (5 mL) at 26 °C. After stirring at 26 °C for 1 h, the resulting suspension was dried under reduced pressure to give a dark brown solid (6.4 mg). Mp: 157-163 °C (decomp.); ¹H NMR (CD₃CN): silent; IR (ATR): ν/cm⁻¹ 3046, 3023, 1607, 1485, 1465, 1418, 1310, 1229, 1164, 1130, 1111, 1077, 1043, 952, 877, 863, 841, 825, 795, 767, 739, 723, 686, 672, 646, 627, 608, 587, 517, 485, 470, 430, 422, 420; LR-MS (FD) *m/z* (%): 532.26 (12), 531.26 (46), 530.25 (M⁺, bp); HR-MS (FD) Calcd. for C₄₂H₂₆: 530.20345; Found: 530.20552.

Recrystallization of the obtained material from dry MeCN/dry THF/dry Et₂O gave dark violet crystals of **1**^{•+}I₃⁻ (at least 0.06 mg, >1%), which were picked up with a needle and characterized by X-ray crystallography. The isolated yield was calculated based on the separated crystals from the as-prepared crystals, which might also contain **1**, **1**^{•+}I₅⁻ (determined by preliminary X-ray analysis), and other forms of cationic species. Mp: 191-196 °C (decomp.); IR (a single crystal, transmission mode): ν/cm⁻¹ 3094, 3045, 2979, 2925, 1955, 1929, 1907, 1819, 1614, 1587, 1530, 1455, 1436, 1345, 1260, 1207, 1166, 1149, 1124, 1084, 1047, 947, 859, 839, 809, 777, 752, 725, 670, 611.

Synthesis of dication salt $1^{2+}(\text{I}_3^-)_2$. **1** (3.00 mg, 5.65 μmol) was added to a solution of iodine (2.15 mg, 16.9 μmol) in dry CH_2Cl_2 (5 mL) at 26 $^\circ\text{C}$. After stirring at 26 $^\circ\text{C}$ for 1 h, the resulting suspension was dried under reduced pressure to give a dark violet solid (5.1 mg). Mp: 177-182 $^\circ\text{C}$ (decomp.); ^1H NMR (CD_3CN): silent (given that the reduction potential of iodine was not sufficient to oxidize radical cation $1^{\bullet+}$ completely, the silent NMR spectrum was attributed to a partial contribution of radical cation $1^{\bullet+}$); IR (ATR): ν/cm^{-1} 3042, 1606 1529, 1513, 1476, 1430, 1419, 1342, 1318, 1229, 1189, 1163, 1128, 1115, 1088, 1040, 990, 952, 941, 874, 859, 840, 811, 796, 774, 768, 751, 721, 711, 693, 676, 657, 627, 610, 551, 517, 469; LR-MS (FD) m/z (%): 532.18 (13), 531.18 (47), 530.17 (M^+ , bp); HR-MS (FD) Calcd. for $\text{C}_{42}\text{H}_{26}$: 530.20345; Found: 530.20499.

Recrystallization of the obtained material from dry CH_2Cl_2 /dry Et_2O gave dark violet crystals of $1^{2+}(\text{I}_3^-)_2$ (at least 0.10 mg, >2%), which were picked up with a needle and characterized by X-ray crystallography. The isolation yield was calculated based on the separated single crystals from the as-prepared crystals, which might contain $1^{\bullet+}\text{I}_5^-$ (determined by preliminary X-ray analysis) or other cationic species.

Mp: 147-153 $^\circ\text{C}$ (decomp.); IR (a single crystal, transmission mode): ν/cm^{-1} 3187, 3078, 3038, 2928, 2855, 1907, 1724, 1646, 1605, 1514, 1471, 1440, 1386, 1358, 1327, 1256, 1198, 1121, 1096, 991, 976, 941, 890, 866, 841, 793, 727, 661, 638.

Data availability

The X-ray data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under reference numbers 2301032-2301035 ($1^{\bullet+}\text{I}_3^-$, main_sample1), 2301036-2301039 ($1^{\bullet+}\text{I}_3^-$, sub_sample2), and 2301040-2301043 ($1^{2+}(\text{I}_3^-)_2$). All other data are presented in the main text or the Supplementary Information.

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Author contributions:

T. Sh., T. Su., and Y. I. developed the concept of this study. T. Sh. and S. K. conducted the synthetic and spectroscopic experiments as well as the theoretical calculations. T. Sh., T. Su., and Y. I. supervised the project. T. Sh. prepared the manuscript with feedback from all authors.

Competing interests: The authors declare the absence of any potentially competing interests.