A soluble pentacene: synthesis, EPR and electrochemical studies of 2,3,9,10-tetrakis(trimethylsilyl)pentacene†‡

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A soluble 2,3,9,10-tetrakis(trimethylsilyl)pentacene (1) was synthesized; the discovery of the radical cationic character of 1 in solution through EPR measurement has provided insights into the sensitivity of acenes towards light and oxygen.

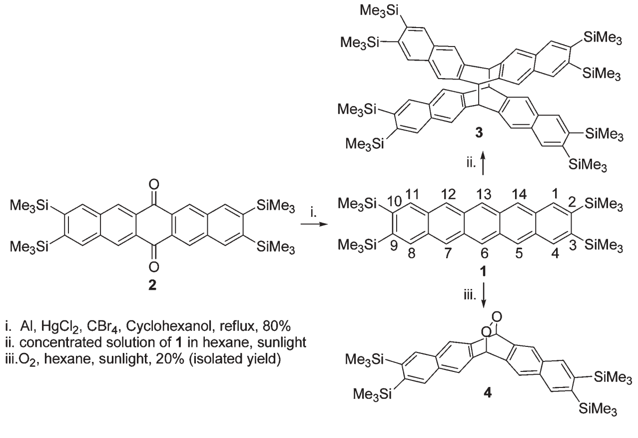
Organic semiconductors have been studied extensively in organic field effect transistors (OFET)[1–7] due to their high mobilities for hole transport (p channel).[8,9] It has also been pointed out that acene derivatives are useful in organic electronics.[10–12] In this connection, a "soluble" and structurally simple pentacene derivative could facilitate a low-cost solution deposition, thereby reducing the cost of the processing step. There are few examples of pentacenes in the literature.[13a,b] Recently, Breen and co-workers have successfully deposited pentacene on a surface by employing a retro-Diels–Alder reaction.[13c] More recently, Wudl and co-workers have synthesized tetramethylpentacene.[13d] Their results prompted us to disclose our recent investigation on the chemistry of "soluble" pentacene. Our approach focuses on the introduction of four lipophilic σ-donating and π-accepting trimethylsilyl groups to the pentacene skeleton. The introduction of the bulky trimethylsilyl groups to pentacene is believed to lead to deaggregation so that its solubility in common organic solvents would be enhanced. Herein we report the synthesis of 2,3,9,10-tetrakis(trimethylsilyl)pentacene (**1**) together with our studies on its chemical and electrochemical properties.

The preparation of **1** involved modifications of a direct-reduction approach of quinone **2**[14a–c] using a carbon tetrabromide-promoted Meerwein–Ponndorf–Verley reduction[14d] (Scheme 1). In this manner, **1** was obtained as a purple-red solid in 80% yield. The hexane solution of **1** was metallic purple-red in color, which deepened with loss of transparency upon concentration. The most attractive feature of **1** is its solubility at room temperature in common organic solvents such as hexane, dichloromethane, benzene, acetone, methanol and ethanol, making **1** a potential candidate in thin-film deposition processes. It is noteworthy that **1** is a highly air- and light-sensitive molecule, so that its isolation and purification must be carried out with a stringent exclusion of air and light using standard Schlenk techniques.

A purified solid-state sample of **1** was found to be stable for 5 days when it was kept in the dark at −4 °C. Whereas a solution of **1** in $CDCl_3$ sealed in an NMR tube in the absence of air was proved to be stable without decomposition over 7 days as monitored by ^1H NMR spectroscopy. Substantial solubility of **1** in $CDCl_3$ facilitates its characterization by NMR spectroscopy at room temperature, which was generally difficult to attain for other pentacene derivatives. The ^1H NMR spectrum of **1** at room temperature showed one single set of resonance signals at δ 8.25, 8.62, 8.96 and 0.48, which are assignable to protons attached to C1, C5, C6 of the pentacene skeleton, and the $SiMe_3$ substituents, respectively. Its ^{13}C NMR, measured also at room temperature, showed six resonance signals at δ 126.2, 126.8, 130.5, 130.7, 136.6 and 140.6 due to six groups of sp^2 carbons and one resonance at δ 1.9 for the $SiMe_3$ substituents. To the best of our knowledge, these data represent the first set of NMR data at room temperature being reported for pentacenes in the literature.

In addition, when we attempted to prepare a single crystal of pentacene under a nitrogen atmosphere, pentacene dimer **3**|| was obtained instead of the pentacene monomer (Fig. 1). The existence of **3** was proved by the ^1H and ^{13}C NMR spectroscopy. The identity of **3** was further supported by the HRMS (APCI) study in that the MH^+ peak of **3** was found.

The reason for the formation of **3** is still unknown to us, but, it is likely that the formation of the dimer may due to the π–π interaction between the pentacene pair. However, there is no sign of such interaction as detected by UV-vis measurement ranging from 0.962×10^{-5} to 8.657×10^{-5} M. Therefore, significant π–π interaction that causes the dimerization may only proceed in a very concentrated environment.



i. Al, $HgCl_2$, CBr_4, Cyclohexanol, reflux, 80%
ii. concentrated solution of **1** in hexane, sunlight
iii. O_2, hexane, sunlight, 20% (isolated yield)

Scheme 1

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b411831f/

‡ This communication is dedicated to Professor Dr. Klaus Hafner on the occasion of his 75th birthday.

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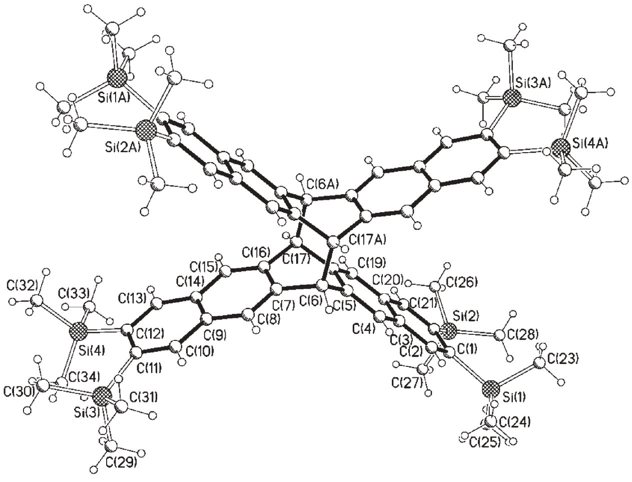


Fig. 1 The X-ray structure of **3**.

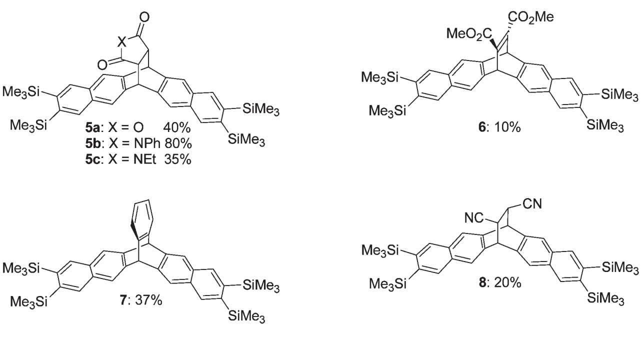
Compound **1** decomposed upon exposure to air in the presence of light to give the peroxide compound **4** (Scheme 1). Interestingly, the ^{1}H NMR signals of **1** broadened during the course of this reaction. This prompted us to investigate the possible involvement of any paramagnetic intermediates in the decomposition mechanism with EPR spectroscopy. Noteworthy is that EPR studies of tetracene[15a] and pentacene[15b–d] in concentrated sulfuric acid have been previously reported. With a vigorous exclusion of oxygen and light, a solution of **1** was EPR silent, which is consistent with a single set of sharp NMR signals observed under these conditions. However, an isotropic resonance centered at g = 2.00,** an indication of $\mathbf{1}^{+\bullet}$, was observed upon an exposure of the solution to air and light. The concentration of the paramagnetic species, however, was very low so that two hundred scans were needed to record a satisfactory signal with an acceptable signal to noise ratio. The splitting pattern of the EPR signal arises from splittings of the unpaired electron due to the three different types of hydrogen atoms on the pentacene moiety.**

Mechanistically, the reaction of **1** with dioxygen may involve single electron transfer from **1** to dioxygen, resulting in the formation of $\mathbf{1}^{+\bullet}$ and superoxide anion radical. However, we are unable to rule out the possibility of an energy transfer pathway from which singlet oxygen may be generated. From our EPR results, a very weak signal of $\mathbf{1}^{+\bullet}$ was observed but we were not able to detect the existence of both superoxide anion radical and singlet oxygen. It is also noteworthy that the likely intermediates, *i.e.*, zwitterionic or diradical species generated through the reaction between singlet oxygen and **1** are EPR-silent, and that prolonged reaction of **1** with dioxygen would lead to the formation of peroxide **4**.

Additional evidence to support the structure of **1** was obtained through its Diels–Alder adducts **5**–**8** (Table 1). It is noteworthy that these reactions were difficult to manipulate due to the reactivity of **1** in solution and must therefore be carried out under low concentration of **1**.

The electrochemical properties of **1** in a CH_2Cl_2–hexane (4 : 1) solvent mixture at 298 K have also been studied by cyclic voltammetry.** The cyclic voltammogram of **1** consisted of a quasi-reversible oxidation wave at 0.25 V and a quasi-reversible reduction wave at −1.81 V. The band gap of **1**, as determined from the oxidation and reduction potentials, was found to be 2.06 V, which is larger than those reported for pentacene and tetramethylpentacene.[13d] The value of 2.06 V corresponds well with the calculated highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gaps which is 2.20 eV for **1**.†† The larger band gap of **1** may be ascribed to the σ-donating and π-accepting properties of the silyl substituents.

Table 1 Diels–Alder adducts of **1**



In conclusion, we have successfully synthesized a pentacene derivative which is soluble in common organic solvents. The property of the compound highlights its potential applications in the thin-film deposition process for organic semiconductors. The discovery of the radical cationic character of **1** in solution has provided insights into the sensitivity of acenes towards light and oxygen. Detailed investigations on the hole transport property of **1** are in progress in our laboratory.

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Notes and references

‖ Crystal data: $C_{40}H_{60}Si_4$, M = 653.24, monoclinic, a = 16.574(4), b = 13.868(3), c = 18.762(4) Å, U = 4291.2(16) Å^3, T = 123 K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 0.162 mm^{-1}, 46139 reflections measured,

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10359 unique ($R_{\mathrm{int}} = 0.0326$) which were used in all calculations. The final $wR(F^2)$ was 0.1915 (all data). CCDC 246839. See http://www.rsc.org/suppdata/cc/b4/b411831f/ for crystallographic data in .cif or other electronic format.

** Experimental details are included in Electronic Supplementary Information (ESI).

†† Orbital energies for 2,3,9,10-tetrakis(trimethylsilyl)pentacene (**1**) were calculated using density functional theory at B3 LYP/6-31G(d)//B3 LYP/6-31(d) level.

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