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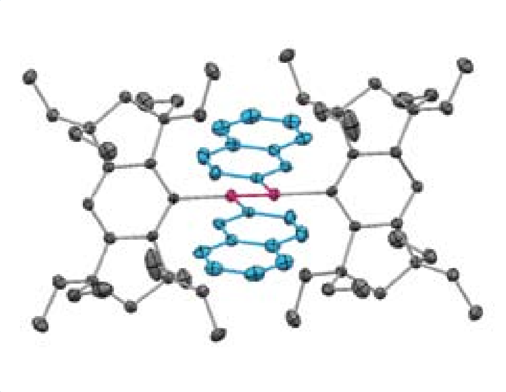

CONTENTS

Research Article

Air-Stable Emissive Disilenes Protected by Fused-Ring Bulky "Rind" Groups

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1. Introduction

The design and improvement of substituents or ligands that play supporting roles in both fundamental and applied chemistry has been a key research theme for many years. In 1981, West and Yoshifuji introduced the concept of kinetic stabilization of the highly reactive Si=Si and P=P double bonds by bulky 2,4,6-trimethlphenyl (mesityl) and 2,4,6-tri-*tert*-butylphenyl (supermesityl) groups, as shown in Figure 1.[1,2] Thereafter, a large variety of unsaturated compounds of the heavier main group elements have been synthesized using the sterically bulky protecting groups.[3] For example, in organosilicon chemistry, silaaromatics (silabenzene),[4] trisilaallenes ($R_2Si=Si=SiR_2$),[5] and disilynes ($RSi{\equiv}SiR$)[6] have been successfully isolated by taking advantage of the steric protection with the appropriate bulky substituents. In 2011, we reported the synthesis and characterization of a cyclobutadiene silicon analog (tetrasilacyclobutadiene) with a planar rhombic charge-separated structure.[7]

Recent efforts have been directed toward investigating the incorporation of unsaturated bonds of the heavier main group elements into carbon π-conjugated systems, because of their potentially useful properties and unique functions, which might offer a way to new elemento-organic hybrid materials.[8] However, this chemistry always suffers from a dilemma. While the steric protection by the bulky groups is essential to stabilize the highly reactive heavier unsaturated bonds, it causes the π-conjugated framework to twist, which reduces the extension of the π-conjugation. A key for the further evolution of this chemistry is to certainly attain a well-defined substituent that can maintain the highly planar π-conjugated framework, as well as providing sufficient steric protection of the heavier unsaturated bonds. This manuscript describes newly developed bulky groups based on a fused-ring octa-R-substituted s-hydrindacene skeleton (Rind groups) and their application to the synthesis of novel air-stable emissive disilenes.

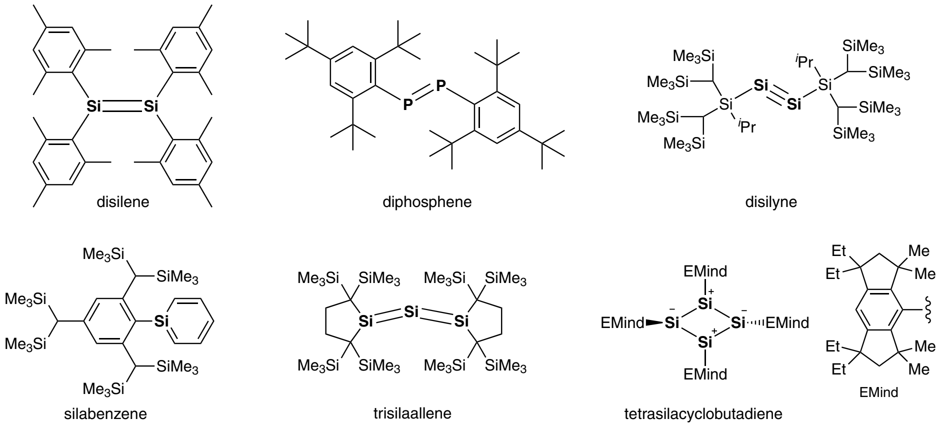

Figure 1. Examples of stable unsaturated compounds of the heavier main group elements.

2. Development of Rind groups

As shown in Figure 2, we have recently focused on the development of a new family of 1,1,3,3,5,5,7,7-octa-R-substituted *s*-hydrindacen-4-yl groups, called the "Rind" groups, where R stands for the initial of the substituents on the four benzylic positions.[9] Significant characteristics of the Rind groups are summarized as follows: (1) The Rind groups can be easily synthesized by the intramolecular Friedel-Crafts reaction. (2) A variety of R-substituents (R^1, R^2, R^3, and R^4) can be introduced at the benzylic positions of the *s*-hydrindacenyl skeleton. (3) The steric effects, and the size and shape variations of the Rind groups can be controlled by the proximate R^3 and R^4 substituents. (4) The physical properties, such as crystallinity or solubility, may be primarily attributable to the peripheral R^1 and R^2 substituents. (5) The Rind groups have a high chemical stability due to the full substitution at all the benzylic positions. (6) The Rind groups can offer an adequate space for the element (E) center; this space is only slightly restricted by the benzylic substituents as a consequence of the *freeze-rotation* fixed in the five-membered fused rings. (7) As another unique feature, the Rind groups have the unsubstituted *para*-position open for further functionalization, thus providing potentially useful *para*-phenylene types of difunctional compounds.

A series of octa-R-substituted bromo-*s*-hydrindacenes, (Rind)Br, can be prepared by a sequence of the Lewis acid catalyzed intramolecular Friedel-Crafts reaction, bromination and vice versa.[9] All the bulky aryl bromides, (Rind)Br, can be transformed into the corresponding bulky aryllithiums, (Rind)Li, as a key reagent for the introduction into various main group elements and transition metals. The abbreviation "Rind" in English demotes the thick outer skin of some types of fruit for protection of the inside fruity flesh. This is totally in accordance with our research concept. In fact, the bulky Rind groups enable us to isolate some new unsaturated compounds of the heavier main group elements, as represented by the π-conjugated disilenes as described below.

3. Air-Stable Emissive Disilenes

We have recently demonstrated a novel class of Si=Si and Si=P compounds, i.e., π-conjugated disilenes and phosphasilenes, by taking advantage of the steric protection with the bulky Rind groups.[8d,8f,10,11] The Rind groups successfully encapsulate the reactive Si=Si and Si=P double bonds and produce the highly coplanar arrangement of the π-frameworks by their perpendicular orientation to and the interlocking proximate R^3 and R^4 substituents above and below the π-frameworks, which are suitable for studying the inherent conjugation properties.

As for the typical examples of the π-conjugated disilenes, Figure 3 shows the two regioisomers, i.e., (*E*)-1,2-di(1-naphthyl)-disilene and (*E*)-1,2-di(2-naphthyl)disilene, protected by the bulky Eind groups (Eind: R^1 = R^2 = R^3 = R^4 = Et). These disilene compounds have been synthesized by the reductive coupling of the corresponding dibromosilanes, (Eind)ArSiBr$_2$ (Ar = 1-naphthyl and 2-naphthyl), with lithium naphthalenide (LiNaph) in THF.[10b,10d] The disilenes have been isolated as red crystals and found to be quite air-stable in the solid state for more than several years with no detectable change, as confirmed by the ^{1}H NMR spectra. They decompose in a dilute hexane solution (*ca*. 10^{-5} mol L^{-1}) upon exposure to air, but slowly with a half-lifetime of *ca*. 2–4 h, much longer than that observed in Tip$_2$Si=SiTip$_2$ (17 min; Tip = 2,4,6-triisopropylphenyl),[12] as estimated by the UV-vis spectroscopy, indicative of the outstanding protection ability of the Eind group. Both the 1,2-di(1-naphthyl)disilene and the 1,2-di(2-naphthyl)disilene exhibit strong π–π* absorptions and distinct emissions at room temperature, both in solution and in the solid state, as shown in Figure 4. The DFT calculations at the B3LYP/6-31G(d,p) level indicate the substantial contribution of the 3p$_\pi$*(Si–Si)–2p$_\pi$*(naphthyl) conjugation.

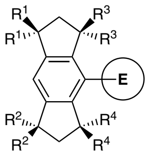

Figure 2. Rind groups.

The X-ray crystallographic analysis of the 1-naphthyl counterpart shows a highly coplanar (*E*)-1,2-di(1-naphthyl)-disilene skeleton, which is favorable for the efficient π-conjugation containing the Si=Si unit, along with a distinct CH/π interaction between the *peri*-H atom of the 1-naphthyl groups and the benzene ring of the perpendicularly-oriented Eind groups.[10d] In the 2-naphthyl counterpart, the Si atoms and the 2-naphthyl groups are disordered over the two positions in the crystal, corresponding to a mixture of two rotational isomers, *s-cis*, *s-cis* and *s-trans*, *s-trans*, in the ratio of *ca*. 6:4.[10b] Each conformer has an essentially coplanar (*E*)-di(2-naphthyl)-disilene framework; thus, only the structure of the *s-trans*, *s-trans* conformer is presented in Figure 3.

The 1,2-dinaphthyldisilenes have a high thermal stability with a decomposition temperature of 245–248 °C for the 1-naphthyl counterpart and 282–285 °C for the 2-naphthyl counterpart under an argon atmosphere. The excellent stability would provide new opportunities for application in a range of organic electronic devices, since the Si=Si units have a smaller HOMO–LUMO energy gap compared to the C=C units. We have demonstrated that the 1,2-di(2-naphthyl)disilene can emit light in an organic light-emitting diode (OLED), as shown in Figure 4.[13] To the best of our knowledge, this is the first experimental observation of electroluminescence (EL) from the heavier group 14 unsaturated compounds, which has opened a new platform for the development of functional elemento-organic materials and devices.

4. Summary

We have described our recent and ongoing work concerning the newly developed fused-ring bulky protecting groups (Rind groups) and their application to the air-stable, room-temperature emissive disilenes. The sterically bulky Rind groups successfully protect the highly reactive Si=Si double bonds, thus providing extraordinarily air-stable disilene derivatives with the highly coplanar arrangement of the π-framework. For example, the (*E*)-1,2-di(1-naphthyl)disilene and the (*E*)-1,2-di(2-naphthyl)disilene demonstrate the strong π–π* absorptions and distinct emission at room temperature, originating from the π-conjugation between the Si=Si double bond and the carbon π-electron system. The unique electronic properties of the π-conjugated disilenes have been determined by spectroscopic methods as well as computational studies. The chemistry of the π-conjugated disilenes has just begun and further investigations are needed for a deeper understanding of their properties and functionalities.

The unique protection ability of the bulky Rind groups also enable us to isolate some other new unsaturated compounds containing the main group elements,[7,14–19] as represented by tetrasilacyclobutadiene, $Si_4(Rind)_4$,[7] germanone, $(Rind)_2Ge{=}O$,[14] and hydro-diboron compounds (Figure 5).[15] The bulky Rind groups have also proven to stabilize some low-coordinate species of transition metals,[20–24] such as mixed diorganocuprates[20] and diorganoiron(II) complexes.[24]

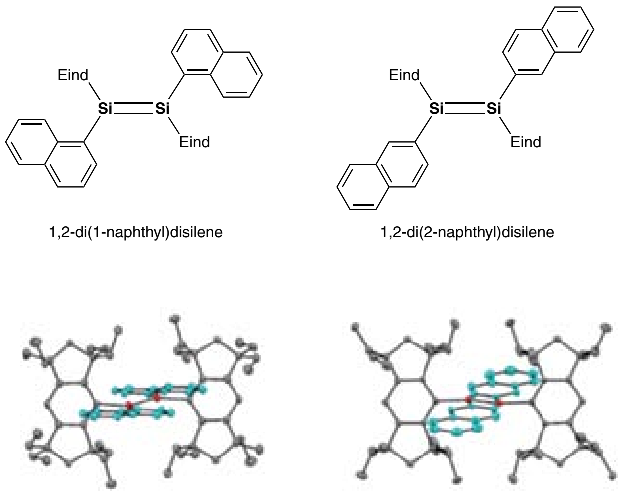

Figure 3. Molecular structures of (*E*)-1,2-di(1-naphthyl)disilene (left) and (*E*)-1,2-di(2-naphthyl)disilene (right).

Figure 4. Solid-state emission of (*E*)-1,2-di(1-naphthyl)disilene (left) and (*E*)-1,2-di(2-naphthyl)disilene (center) at room temperature in the open air. EL of (*E*)-1,2-di(2-naphthyl)disilene (right).

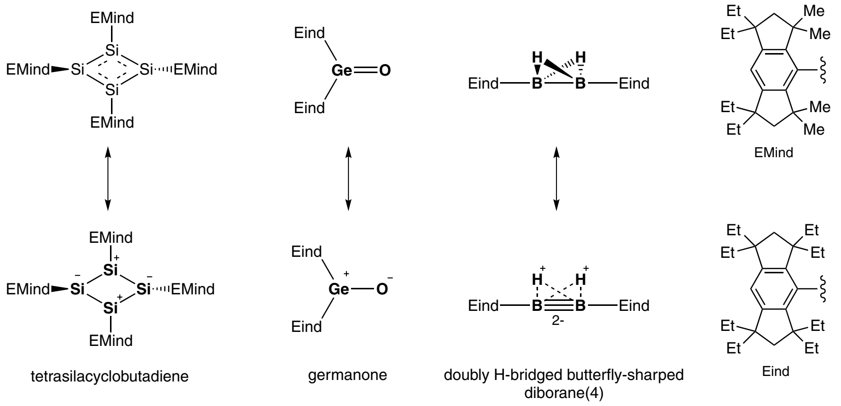

Figure 5. Examples of new unsaturated compounds of the main group elements stabilized by the bulky Rind groups.

The availability of stable low-coordinated species provides a new clue to the full understanding of the bonding nature of the heavier unsaturated compounds, as well as to various reactivities under ambient conditions, which would open a new facet to the chemistry of the main group elements.[25]

Acknowledgement:

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Tsukasa Matsuo graduated from Tohoku University with B. Science (1994) and M. Science (1996) degrees under the direction of Prof. Hideki Sakurai and Prof. Mitsuo Kira. He received his Ph.D. (1999) from University of Tsukuba supervised by Prof. Akira Sekiguchi. He became Assistant Professor at Tsukuba Advanced Research Alliance (TARA) in 1999. He moved to the Institute for Molecular Science (IMS) as Assistant Professor (2001) to study with Associate Professor Hiroyuki Kawaguchi. In 2007, he moved to RIKEN as Deputy Unit Leader to study with Prof. Kohei Tamao, the Unit Leader. In 2012, he was appointed to his current position as an Associate Professor at Kinki University. He has received the Inoue Research Award for Young Scientists (2001), the BCSJ Award (the Chemical Society of Japan) (2001), the Chemical Society of Japan Award for Young Chemists (2003), the Incentive Award (the Society of Silicon Chemistry) (2010), and the BCSJ Award (the Chemical Society of Japan) (2011).
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B4380	Eind-Br	5g	1g

Compounds Composed of Two Elements (1)
Halocarbons

Kentaro Sato

Carbon can form stable structures of any length, can bond with many other elements, and can form single, double, and triple bonds. Needless to say, these unique characteristics of carbon are the foundation of the chemical diversity in this world. In fact, one can think of virtually infinite number of compounds from just the combination of two elements, carbon and hydrogen.

Take simple alkanes as examples. The number of isomers is calculated to be 75 for decane (C10), 366,319 for icosane (C20), and 4,111,846,763 for triacontane (C30) (Note, however, that these numbers do not include enantiomers and other stereoisomers. They are also theoretical numbers, meaning that they count isomers that cannot actually exist for reasons such as excessive steric hindrance.) When additional factors like multiple bonds and cyclic structures are taken into account, it is not difficult to imagine how astronomically huge the number of hydrocarbons can be.

Fluorocarbons

In terms of chemical diversity, the combination of which two elements do you think comes in second behind hydrocarbons? The first one to come to your mind may be the carbon-halogen combination. For instance, fluorine has a similar atomic radius to hydrogen and C-F bond is also extremely strong, so fluorocarbons have a possibility to form as many compounds as hydrocarbons.

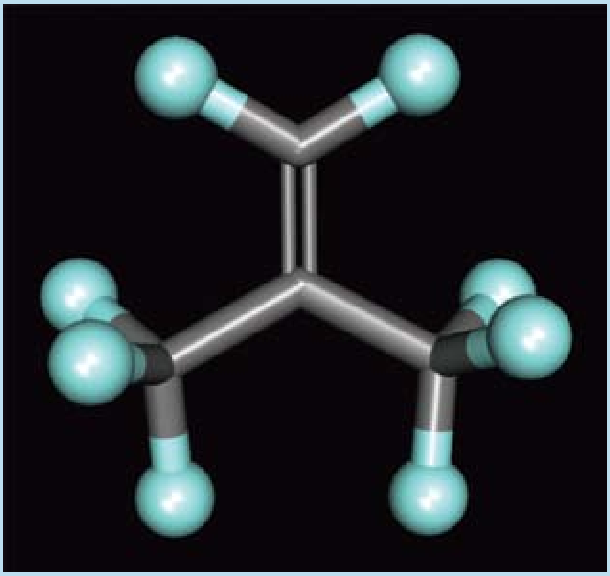
Fluorocarbons were synthesized in 1926 for the first time. The fact that it took 40 years after the isolation of fluorine is probably a testament to how difficult the handling of elemental fluorine was. The first fluorocarbon synthesized was the simplest of them all, carbon tetrafluoride (CF_4).

In 1938, Teflon was serendipitously discovered in the laboratory of DuPont, when a sample of tetrafluoroethylene ($F_2C{=}CF_2$) stored in a metal cylinder was found to have polymerized. Teflon is resistant against thermal and chemical stresses as well as having very low friction. These properties have made it an essential coating material for household commodities such as kitchenware as well as laboratory equipment.

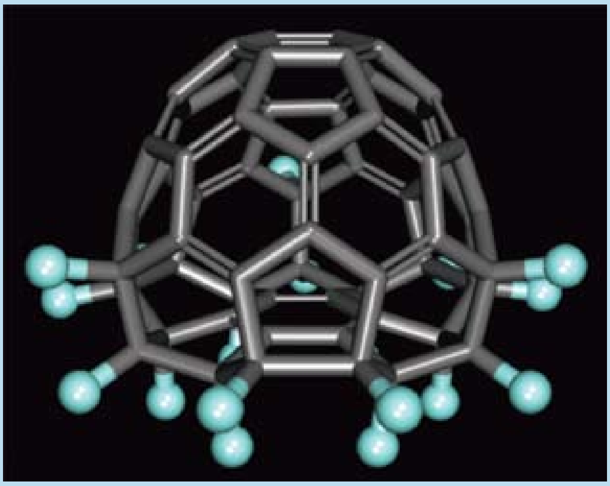
Perfluorinated alkanes started to draw the interest of organic chemists with the introduction of the field called fluorous chemistry. Highly fluorinated (“fluorous”) compounds tend to be insoluble in common organic solvents and water but soluble in perfluoroalkane solvents. This is a useful property in terms of the isolation of relevant compounds. As fluorous solvents, perfluorohexane ($F_3C(CF_2)_4CF_3$) and perfluorotoluene ($C_6F_5CF_3$) are used frequently.

Some of these fluorocarbons, however, possess strong biological toxicity. For example, perfluoroisobutene is about ten times more toxic than phosgene and is even included in the list of substances regulated by the Chemical Weapons Convention. The high electronegativity of fluorine makes perfluoroisobutene a potent electrophile that can damage organs such as the lungs. One must always be aware of the potential toxicity of polyfluoroolefins when there is a need to use them.

Fluorinated fullerenes are worth mentioning as unique examples among fluorocarbons. For instance, the Russian research team led by Olga V. Boltalina has reported a number of halogenated fullerenes which they synthesized by treating fullerene with various halogenation reagents. As shown below, in a molecule of $C_{60}F_{18}$ the attachment of 18 fluorine atoms has resulted in this humorous shape reminiscent of jellyfish.



Perfluoroisobutene



$C_{60}F_{18}$ has a humorous shape reminiscent of jellyfish

Chlorocarbons

How about the combination of C-Cl, with chlorine being a size larger than fluorine in the periodic table? It may appear that one could make as many compounds as fluorocarbons, but it turns out that it is not the case in reality. As for perchloroalkanes, perchlorobutane containing only 4 carbons is the largest that has ever reported. The fact that C-Cl bond is much weaker compared with C-H and C-F bonds coupled with other reasons such as the large atomic radius of chlorine causing steric hindrance seem to prevent larger perchloroalkanes from existing as stable compounds.

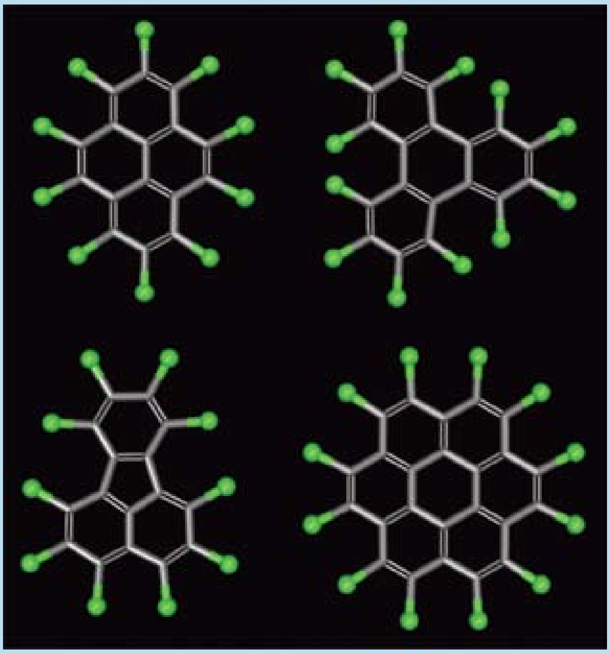
Among chlorocarbon compounds, carbon tetrachloride and tetrachloroethylene are familiar to chemists as solvents. But of course, these chlorinated solvents are getting more and more strictly regulated due to their toxicity and negative environmental impact.

Unlike perchloroalkanes, many perchlorinated derivatives of aromatic compounds are known thanks to reduced steric hindrance among the chlorine atoms. Hexachlorobenzene (C_6Cl_6) was once used as an agricultural pesticide and an antiflamming agent for clothes, but it is banned today because of its carcinogenicity.

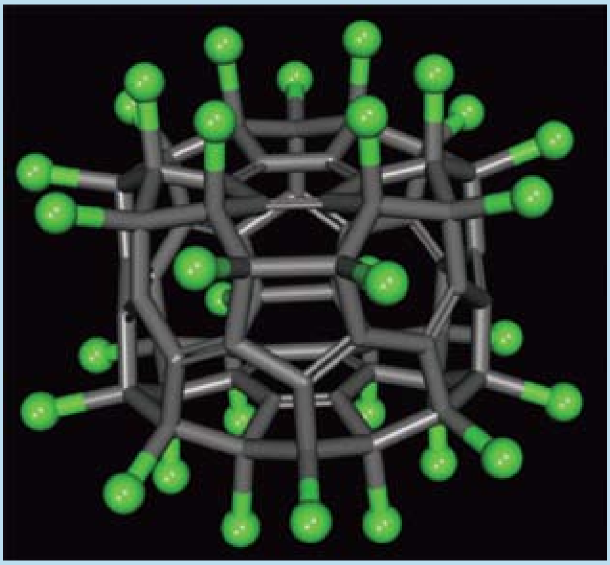
In addition to hexachlorobenzene, perchlorinated versions of pyrene, triphenylene, fluoranthene, and coronene have been synthesized.

Like the aforementioned fluorinated fullerene, there are interesting chlorinated fullerene derivatives. For example, the treatment of fullerene with antimony pentachloride yielded several chlorinated fullerenes, of which $C_{60}Cl_{30}$ has a drum-like shape as shown in the figure below.

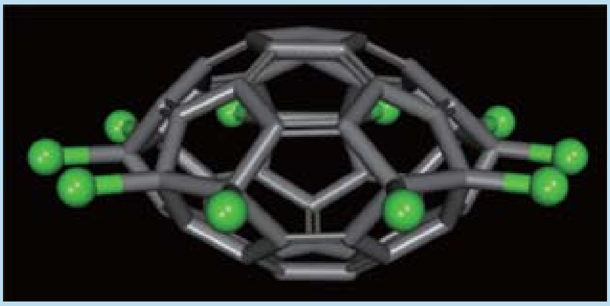
$C_{50}Cl_{10}$ is another example which was synthesized in 2004. This one looks kind of like Saturn as shown below. C_{50} fullerenes are usually too strained to be isolated. However, this rare C_{50} derivative was directly obtained by the arc discharge synthesis in the presence of carbon tetrachloride. Looking at these structures reminds us that the chemical space can be endlessly large even with the combination of just two elements.



Perchlorinated versions of pyrene, triphenylene, fluoranthene, and coronene



$C_{60}Cl_{30}$ has a drum-like shape



Rare C_{50} fullerene derivative $C_{50}Cl_{10}$

Bromocarbons

The actual examples of C-Br compounds are much more limited, due to the large atomic radius of bromine (even larger than chlorine) and weaker C-Br bonds. Therefore, carbon tetrabromide (CBr_4) and hexabromoethane (C_2Br_6) are the only known examples of perbromoalkane.

In organic synthesis, carbon tetrabromide is often used with triphenylphosphine to brominate primary alcohols under mild conditions. It is something that all synthetic chemists should remember as a useful reagent.

Aside from them, only a few compounds are known including tetrabromoethylene (C_2Br_4) and hexabromobenzene (C_6Br_6). The latter is sometimes used as a starting material of polycyclic aromatic hydrocarbons and liquid crystalline materials, since it can be functionalized in six directions by reactions such as cross coupling.

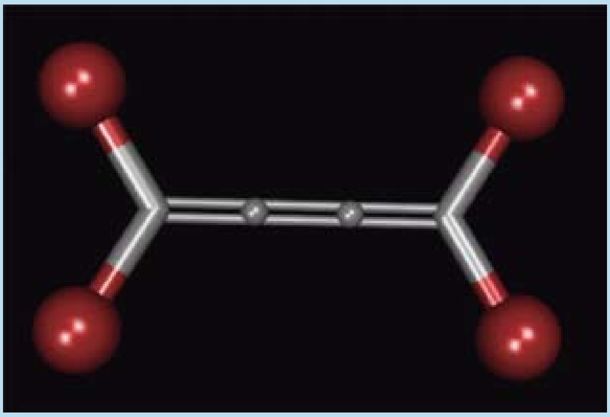
There are interesting halogenated carbon compound families such as perhaloallenes ($X_2C=C=CX_2$) and perhalobutatrienes ($X_2C=C=C=CX_2$). The last one that was synthesized among these was tetrabromobutatriene, which was synthesized in 2004 by adding bromine to dibromobutadiene (BrC≡C-C≡CBr) at low temperature.

As for fullerene derivatives ($C_{60}Br_n$), examples with n=6, 8, 24 are known. In 2012, chlorinated and brominated versions of graphite were synthesized by treating graphite with liquid chlorine and bromine under microwave irradiation conditions. Besides the interest on their electronic properties, there have been growing expectations that these materials could be elaborated further to prepare graphene derivatives containing various functional groups.

Iodocarbons

Iodine has a particularly large atomic radius and therefore makes very limited numbers of compounds with carbon. Carbon tetraiodide (CI_4) is the only periodoalkane ever known. Like the bromine counterpart, it is used for iodination reactions but is also known to decompose easily by the effect of light and heat.

Similar to bromine, C-I compounds such as tetraiodoethylene (C_2I_4), hexaiodobenzene (C_6I_6), tetraiodoallene ($X_2C=C=CX_2$), and tetraiodobutatriene



Tetrabromobutatriene ($Br_2C=C=C=CBr_2$)

($X_2C{=}C{=}C{=}CX_2$) are known. Under extremely highly pressurized conditions of about 35 GPa, hexaiodobenzene is known to undergo metallization, turning from an insulator into a good electric conductor while maintaining its molecular state. It is known to even become a superconductor at ultralow temperatures near 2 kelvins.

As we have seen, the chemical space composed of just the combination of carbon and halogens can be really deep. Next time, let us continue this line of thought and move on to the combinations of carbon-nitrogen, carbon-oxygen, and more.

Introduction of the author :

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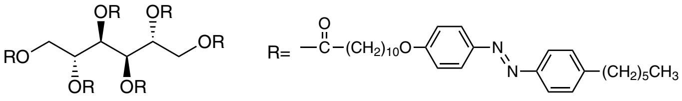
[Brief career history] He was born in Ibaraki, Japan, in 1970. 1995 M. Sc. Graduate School of Science and Engineering, Tokyo Institute of Technology. 1995-2007 Researcher in a pharmaceutical company. 2008-Present Freelance science writer. 2009-2012 Project assistant professor of the graduate school of Science, the University of Tokyo. 2014-present Publicist for π-system figuration, scientific research on innovative areas.
[Specialty] Organic chemistry
[Website] The Museum of Organic Chemistry <http://www.org-chem.org/yuuki/MOC.html>

Organic Material with Photochemically Reversible Liquefaction and Solidification

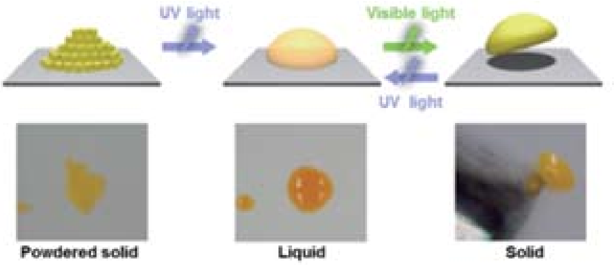
H1452 1,2,3,4,5,6-Hexa-*O*-[11-[4-(4-hexylphenylazo)phenoxy]undecanoyl]-D-mannitol (1)

1g, 5g

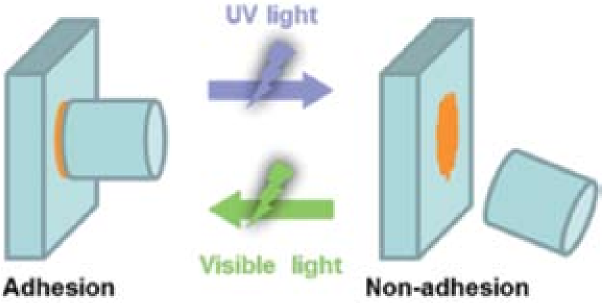


1

1,2,3,4,5,6-Hexa-*O*-[11-[4-(4-hexylphenylazo)phenoxy]undecanoyl]-D-mannitol (**1**), developed by Akiyama, Yoshida, is a liquid-crystalline compound having a skeleton of sugar alcohol and azobenzene groups. **1** shows the photo-reactivity of liquefaction by UV light and solidification by visible light at room temperature, and can be repeatedly liquefied and solidified. The use of **1** is expected to apply to reusable photo-reversible adhesives.



Liquefaction of the solid by UV light irradiation, and solidification by visible light irradiation (provided from AIST)



View of photo-reversible adhesion and non-adhesion

*This product receives a license of invention of Advanced Industrial Science and Technology (AIST) (Jpn. Patent Appl. 5360794). If you use it for industrial purposes, please contact us.

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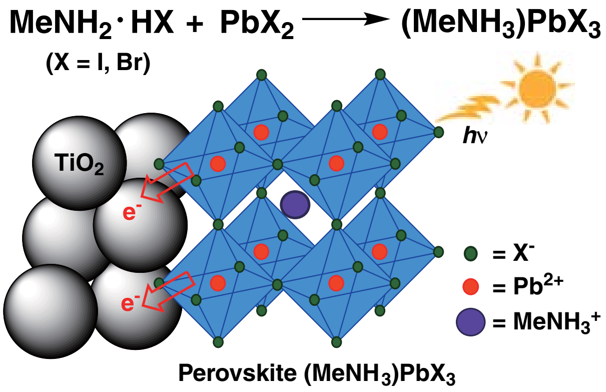
Reagents for Organic-Inorganic Perovskite, $(MeNH_3)PbX_3$

M2556	**Methylamine Hydroiodide (1)**	**1g, 5g, 25g**
M2589	**Methylamine Hydrobromide (2)**	**1g, 5g**

$MeNH_2 \bullet HI$ (**1**)

$MeNH_2 \bullet HBr$ (**2**)

Perovskite solar cells, the so-called organic-inoganic hybrid solar cell, which were first reported in 2009 by Miyasaka *et al.* recently received much attention.1) The organic-inorganic perovskite crystal, $(MeNH_3)PbI_3$, can functionalize as a visible light sensitizer toward titanium dioxide. In the solar cell device with a hole transport material (eg. Spiro-OMeTAD), the energy conversion efficiency has been more than 15% so far, thus it is greater than those of organic photovoltaics (OPV) and dye-sensitized solar cells (DSSC).2,3) The perovskite solar cell is able to output more than 1 V, because the perovskite compound shows strong absorptivity of light and then efficiently transports both electron and hole carriers without their recombination. A device of the perovskite solar cell can be fabricated by a solution process for manufacturing at low cost. A modification of X in the $(MeNH_3)PbX_3$ can control the band gap and range of absorption wavelength. The perovskite compound with X = Br is useful for photo absorption in shorter wavelengths (<560 nm) and the compound with X = I is relatively useful for that in longer wavelengths up to 800 nm.1) Methylamine hydroiodide (**1**) or methylamine hydrobromide (**2**) is reacted with lead(II) halide to give the corresponding organic-inorganic perovskite compound, $(MeNH_3)PbX_3$ (X = Br or I).



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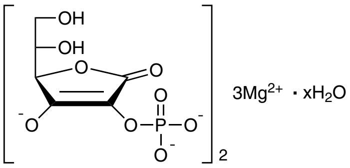
Vitamin C Derivative

A2521 L-Ascorbic Acid 2-Phosphate Sesquimagnesium Salt Hydrate (1) 5g, 25g



1

Since Martin successfully isolated and established pluripotent cell lines with the properties of teratocarcinoma stem cells directly from normal early mouse embryos *in vitro*,1) research on embryonic stem (ES) cells has progressed year after year.

In 2006, S. Yamanaka *et al*. identified factors for inducing pluripotent stem cells from somatic cells.2) Since then, technologies to establish induced pluripotent stem (iPS) cells have been developed.
Recently, ascorbic acid was found to enhance the generation of iPS cells3) and the cardiac differentiation of ES cells4) and iPS cells.5) Ascorbic acid 2-phosphate is a stable derivative of ascorbic acid and has been used as a supplement instead of ascorbic acid.6,7) The application of ascorbic acid 2-phosphate for the field described above has been demonstrated, i.e. serum-free culture,8) feeder-independent culture,9) *etc*.

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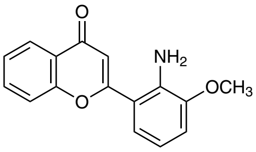
MEK Inhibitor

A2529 2-(2-Amino-3-methoxyphenyl)chromone (= PD 98059) (**1**) 10mg



1

The homeodomain protein Nanog plays an essential role in the self-renewal of embryonic stem (ES) cells.1-3) On the other hand, it was reported that Nanog gene repression was primarily mediated by the Grb2/Mek pathway.4) 2-(2-Amino-3-methoxyphenyl)chromone (PD 98059, **1**) is a MAPK/ERK kinase (MEK) inhibitor5,6) and used as one of the biologically active small molecules in the study described above.4)

Grb2: growth factor receptor-bound protein 2
MAPK: mitogen-activated protein kinase
ERK: extracellular signal-regulated kinase

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