Crystal Structure of a Silyl Cation with No Coordination to Anion and Distant Coordination to Solvent

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The crystal structure of a stable silyl cation, triethylsilylium, in the form of its tetrakis(pentafluorophenyl)borate salt $[Et_3Si^+\ (C_6F_5)_4B^-]$ (Et, ethyl) shows no coordination between cation and anion. The closest silicon-fluorine distance is greater than 4 angstroms. A toluene solvent molecule is close enough to cause some deviations from planarity at the silicon, but the silicon-toluene distance is well beyond the sum of the silicon and carbon covalent radii. The toluene molecule is essentially planar and undistorted, as expected if little or no positive charge has been transferred from silicon to toluene.

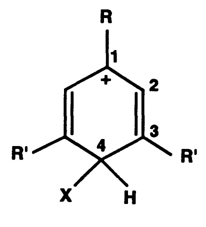
For almost half a century (*1*), chemists have endeavored to create a positive ion chemistry for silicon (R_3Si^+) analogous to that of carbocations (R_3C^+). Theory predicts that silyl cations are stable, even more so than analogous carbocations, because of the larger size, polarizability, and electropositivity of silicon (*2*). Moreover, such species have been studied thoroughly in the gas phase (*3*), and recent studies have provided evidence for their existence as reactive intermediates (*4*). Many reports of direct observation of stable, long-lived silyl cations in condensed phase have been flawed (*5*) and continue to be controversial (*6–8*).

We report the crystal structure of Et_3Si^+ $(C_6F_5)_4B^-$, triethylsilylium tetrakis(pentafluorophenyl)borate, which incorporates a stable silyl cation. The pervasive problem in the characterization of stable silyl cations has been separation of the cation from the anion (*9*) and from the solvent (*10*). We prepared this material in the same fashion as in our past solution studies (*7*), by reaction of a trityl salt with a silane (Ph, phenyl)

$$Ph_3C^+\ X^- + R_3Si\text{–}H \rightarrow Ph_3C\text{–}H + R_3Si^+\ X^- \qquad (1)$$

The stronger C-H bond replaces the weaker Si-H bond. Previous studies indicated that a variety of anions (X^-) were unsuitable in the solid phase because of instability or strong coordination: ClO_4^-, $CF_3SO_3^-$, N_3^-, Ph_4B^-, and (m-di-CF_3-C_6H_3)$_4B^-$ (*7, 9, 10*). We selected $(C_6F_5)_4B^-$ because it showed very low coordinating ability with zirconium and thorium (*11*). Nuclear magnetic resonance (NMR) studies in a variety of solvents indicated that the least coordinating solvents are aromatic hydrocarbons (*12*). Removal of the solvent left a solid from which we could remove the by-product triphenylmethane by washing it with hexane. We examined several organic substituents (R) and, because of the stability and ^{29}Si NMR properties of its salt, chose ethyl for crystallographic studies. We recrystallized Et_3Si^+ $(C_6F_5)_4B^-$ from mixtures of hexane and toluene and solved the structure (*13*) (Fig. 1).

Previously reported structures of candidates for silyl cations in the solid had silicon covalently bonded to perchlorate, pyridine, acetonitrile, or a brominated carborane (*9, 14, 15*), the Si-O or Si-N bond being within 0.1 Å of the normal length and Si-Br within 0.2 Å. In contrast, the anion and cation in the present structure are well separated. The closest approach is a Si-F distance of 4.04 Å, well beyond a range of significant interaction. The unit cell contains two toluene molecules per silyl entity. The toluene molecules are essentially unperturbed geometrically, indicating little bonding interaction with Si. A full bond from Si to a para C (C-4) would resemble a Wheland σ complex (X = Et_3Si, R = CH_3, R′ = H)



Crystallographic models for such species have been reported: for example, X = CH_3 and R,R′ = pyrrolidino (*16*), which has an sp^3 C-4 (∠343′ = 113° and ∠34X = 109°), severe aromatic C-C bond alternation (bond lengths: 3-4 = 1.515 Å, 2-3 = 1.385 Å, and 1-2 = 1.425 Å), and considerable deviation of C-4 from the plane of the other carbons (CCCC dihedral angles: 18.5° for 2343′, 6.9° for 1234, and 6.5° for 1′123). In contrast, the toluene that is closest to silicon is essentially undistorted: the geometry at C-4 is close to sp^2 (∠343′ = 118° and ∠34H = 120.5°), the aromatic C-C bond lengths are very similar (bond lengths: 3-4 = 1.40 Å, 2-3 = 1.37 Å, and 1-2 = 1.38 Å), and the ring is very close to planarity (largest dihedral angle 3°). In comparison with the true σ complex, such structural parameters provide no support for significant σ complexation, so that little or no positive charge has moved from Si to C. Moreover, the distance from Si to the para C, 2.18 Å, is almost 0.35 Å longer than the normal 1.85 Å, is well outside the range (1.9 to 2.0 Å) of "long" Si-C bonds that usually involve Si-*tert*-butyl, and is 0.30 Å beyond the sum of the C and Si covalent radii (1.88 Å) (*17*). From the long Si-C distance and the absence of distortion in toluene, we conclude that covalent bonding between Si and a solvent C, if present, is very weak.

The presence of the toluene molecule nonetheless pushes the three ethyl groups back slightly so that the geometry about Si is not planar. The average C-Si-C angle is 114° (range: 112.8° to 114.9° for the six angles in the crystallographically distinct molecules) rather than 120°. Thus the pseudosymmetry around silicon is C_{3v} rather than D_{3h}, and the distance of Si from the plane of the three methylene C atoms is 0.4 Å. Steric and electrostatic interactions are important here, as the ethyl groups are nonequivalent and are carefully arranged to avoid steric interactions with each other and with the toluene. Because covalent bonding is weak or absent between Si and toluene, the deviations from planarity probably arise from a combination of steric effects, long-range orbital interactions, and crystal packing forces. It is critical to realize that, in contrast to C, there are no compelling electronic forces to maintain planarity around Si. For carbocations and carbon radicals, planarity optimizes π conjugation with aro-

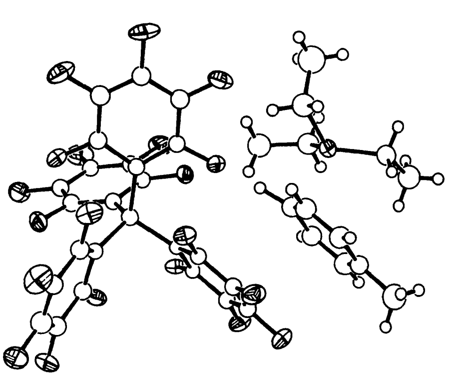


Fig. 1. Molecular structure of triethylsilylium tetrakis(pentafluorophenyl)borate, Et_3Si^+ $(C_6F_5)_4B^-$. Silyl cation, upper right; anion, left; the closer toluene solvent molecule, lower right.

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matic rings and hyperconjugation with alkyl groups. Because conjugation and hyperconjugation are much weaker for Si than for C (Si=C versus C=C), such effects do not provide the restoring forces to maintain planarity around Si that are present in C systems. These effects have been previously recognized in silyl radicals. Whereas carbon radicals tend to be planar, analogous silyl radicals are nonplanar: for example, $Me_3Si\cdot$ has an out-of-plane angle of about 15° (*18*). In the same manner, the silyl cation herein easily distorts from the plane to relieve external sources of strain. This distortion explains why the ^{29}Si NMR chemical shift ($\delta = 92.3$ in benzene) moves ~90 parts per million (ppm) (*12*) from the position of the hydride ($\delta = 0.2$) rather than the 300 ppm or so expected for a planar structure (*8*). Chemical shift is extremely sensitive to such geometrical distortions. It is possible that the use of π-conjugating or more bulky substituents could bring the geometry around Si closer to planarity. This structure, albeit nonplanar, is best termed a stable silyl cation because it entirely lacks coordination to the anion, the distance to the weakly coordinating toluene is unprecedented for bonding, and the toluene lacks any of the geometric characteristics of a σ complex.

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13. A colorless, prismatic crystal (approximate dimensions, 0.26 mm by 0.48 mm by 0.14 mm) was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection corresponded to a triclinic cell with a = 13.168(4) Å, b = 17.593(3) Å, c = 18.117(4) Å, V = 4131(3) Å^3, α = 86.19(2)°, β = 84.21(2)°, and γ = 82.24(2)°, where the number in parentheses is the error in the last digit. For number of molecules in the unit cell Z = 4 and formula weight = 974.56, the calculated density is 1.567 g cm^{-3}. Data were collected at −120° ± 1°C with the ω-θ scan technique to a maximum 2θ value of 48.0°. From 4627 observed reflections, the structure was solved by direct methods (SHELXS-86) in the space group $P\bar{1}$. The unit cell contained four molecules of $Et_3Si^+ (C_6F_5)_4B^-$ (two of which were crystallographically distinct from the other two) and eight molecules of the solvent, toluene. Only silicon and fluorene were refined anisotropically. Hydrogen atoms were included as fixed contributors at calculated positions, except for the hydrogen on the para carbon of the toluene closer to Si. The final cycle of full-matrix, least squares refinement led to unweighted and weighted agreement factors of R = 0.069 and R_w = 0.666. All calculations were done with TEXSAN software.
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Optically Active Carbon: Kinetic Resolution of C_{76} by Asymmetric Osmylation

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The chiral fullerene C_{76} was kinetically resolved by asymmetric osmylation providing an example of an optically active allotrope of a pure element. C_{76} recovered from the treatment of racemic C_{76} with OsO_4 and a chiral alkaloid ligand, showed a specific rotation $[\alpha]_D$ of −4000° (>97 percent enantiomeric excess) and a circular dichroism spectrum corresponding to the ultraviolet spectrum. Regenerated C_{76} formed by reducing the asymmetrically osmylated C_{76} with $SnCl_2$ was enriched in the opposite enantiomer. Analysis of the local curvature of the C_{76} molecule indicated that OsO_4 should selectively add to 2 of the 30 types of bonds in C_{76}. This regioselectivity was supported chromatographically and interpreted in terms of the kinetic resolution.

The double-helical fullerene C_{76} has been described as "one of the most fascinating molecular architectures ever seen in nature" (*1*). This chiral allotrope of carbon has been isolated in racemic form as a minor component of Krätschmer-Huffman soot (*1*, *2*). Numerous attempts to resolve C_{76} into its enantiomers by classical means have not been successful. Here we report the kinetic resolution of C_{76} by asymmetric osmylation whereby the enantiomers of C_{76} are discriminated chemically, producing an optically active sample of elemental carbon.

We have shown that fullerene osmylation is selective with respect to stoichiometry (*3*, *4*), regiochemistry (*5–7*), and stereochemistry (*8*). The kinetic resolution of C_{76} combines all of these attributes, one enantiomer of the substrate reacting faster with an asymmetric reagent than the other enantiomer. The starting material becomes enriched in the less reactive enantiomer, and the reaction product corresponds to the more reactive enantiomer (*9*). We have shown that Sharpless' cinchona alkaloid-derived ligands for the asymmetric dihydroxylation of olefins (*10*, *11*) can be used for the asymmetric bisosmylation of C_{60} giving chiral $C_{60}(OsO_4py_2)_2$ isomers with optical rotations up to 3700° (*8*). A potential difficulty with C_{76} is one of regiochemistry, C_{76} contains 30 types of carbon-carbon bonds, and reaction at different bonds could give different enantiomer discriminations which might oppose each other. Considering that C_{76} is most likely to osmylate at the fusion of two six-membered rings, as found for C_{60} (*5*, *6*), this still

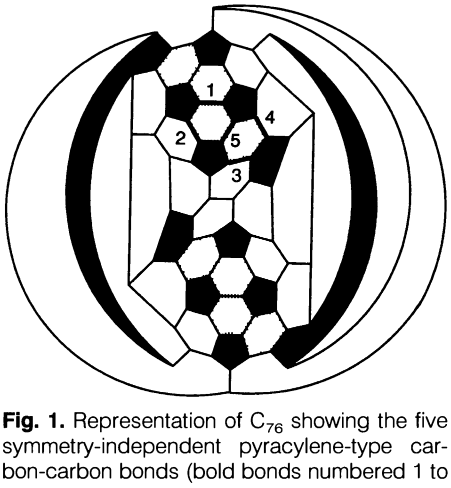

Fig. 1. Representation of C_{76} showing the five symmetry-independent pyracylene-type carbon-carbon bonds (bold bonds numbered 1 to 5) which combine to give reactive chrysene-shaped units (shaded). Five-membered rings are blackened.

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