Triethylsilyl Cations

In their recent report (1) about the crystal structure of the compound

\[(\text{C}_2\text{H}_3)_2\text{Si}^+\text{(C}_2\text{H}_5)_4\text{B}^-(\text{C}_6\text{H}_5\text{CH}_3)_2\]

J. B. Lambert et al. conclude that the silyl cation is essentially isolated and that the Si atom forms only three bonds (to C atoms of the ethyl groups). Analysis of the values of interatomic distances and bond angles on the basis of structural principles (2), however, indicates that there is a fourth bond of significant strength to the para C atom of an adjacent toluene molecule and that a good fraction (35%) of the positive charge of the cation is transferred to the toluene molecule.

The reported distance (1) between the Si atom and the para C atom of the toluene molecule is 2.18 Å, which is 0.24 Å greater than the sum of the single-bond covalent radii of C (0.77 Å) and Si (1.17 Å) (2, p. 224). The sum of these radii, 1.91 Å, agrees well with the Si-C distances observed in silicon carbide and compounds of Si and the tertiary butyl radical, but smaller values result from hyperconjugation (2, pp. 308-309) involving hydrogen atoms attached to the C atom; there is a decrease of roughly 0.03 Å for each hydrogen atom: 1.91 Å for isopropyl, 1.88 Å for ethyl, and 1.85 Å for methyl. A single covalent bond from Si to C₄ of toluene (with only hydrogen atom attached) would have a length of 1.91 Å; the observed value is 2.18 Å, which is 0.27 Å greater. With use of the well-established equation (2, p. 255)

\[D(n) = D(1) - 0.60 \log n\]

this difference leads to \(n = 0.35\) for the bond number.

Lambert et al. state that the observed Si-C bond length to C₄ of the toluene molecule is so much greater than the single-bond covalent value that one can conclude that this bond, if it is present at all, is very weak. The value \(n = 0.35\) found by application of the bond length equation does not correspond to this description. It has been my experience that calculated bond numbers as small as 0.10 (which represent an increase of bond length as great as 0.60 Å) need to be taken into consideration.

Some support for a large value of \(n\) is provided by the observed values of the C-Si-C angle of the pyramidal Si(C₂H₅)₃ group, 114°, and the height of the Si atom above the plane of the three C atoms, 0.4 Å. Both of these values are closer to those for tetrahedral Si than to those for a planar group, which suggests a value of \(n\) greater than 0.5.

For \(n = 0.35\), the expected distortions of the toluene \(C_6\) ring are only about 0.02 Å (1, p. 237) and accordingly are difficult to detect.

It is my conclusion, contrary to that of Lambert et al., that the positive electric charge of the silyl cation is not essentially restricted to this cation in this crystal, but is instead (to the extent of about 35%) distributed also over the atoms of the adjacent toluene molecule.

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REFERENCES


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J. B. Lambert et al. report (1) the crystal structure of triethylsilyl tetrakis(pentafluorophenyl)borate prepared from toluene solution, and they characterize it as being a somewhat nonplanar triethylsilylenium ion with a noncoordinating anion and as having only distant, weak coordination with toluene, which is incorporated in the crystal lattice. Lambert et al. ascertain that the observed 2.18 Å distance between Si and para C of toluene is too long for \(\sigma\)-bonding interaction, and they suggest that the observed nonplanarity of the free triethylsilylenium ion results from weak interaction with toluene, which causes distortion. However, if the triethylsilylenium ion could exist as a long-lived species, it is inconceivable that it could not react with toluene (a good \(\pi\)-base). To probe this question, we repeated the work of Lambert et al. and obtained the reported ionic complex. When the complex was quenched with a hindered base besides hexaethyldisiloxane, we then obtained triethylsilyltoluenes, albeit in low (7%) yield. This result is in accord with the formation of the intermediate triethylsilyltoluenium ion which, on competing deprotonation with desilylation, gives the silylated toluenes. Subsequently, we have fully optimized the geometry of the \(\rho\)-triethylsilyltoluenium ion (Fig. 1) with the use of the Gaussian-92 series of programs at the HF/6-31G* level, and we calculated its structural parameters and the expected \(29\)Si chemical shift with the use of the IGLO method (2).

The calculated bond lengths (Å) and bond angles (Fig. 1) agree well with the reported (1) experimental crystal structure data. Whereas the calculations (Fig. 1) refer to gas phase ions, close agreement was found between calculated and observed (carbocation chemistry) structures. Compared to toluene itself, \(\sigma\)-complexed toluene in the crystal structure was clearly deformed. The Si-C bond length of 2.18 Å (experimental) and 2.197 Å (theoretical) in the Wheland complex, as compared with a normal Si-C covalent bond distance of 1.85 Å, could be explained by the contribution of \(\beta\)-silicon hyperconjugation.

In the search for stable, long-lived carbocations, differentiation of de facto alkyl cations from polarized donor-acceptor complexes has been possible primarily through study of the involved carbocationic carbon centers with the use of \(^{13}\)C nuclear magnetic resonance (NMR) (3). Similar consideration is also valid for trialkylsilyl cations. An R₃Si⁺ ion should show very highly deshielded \(29\)Si resonance. Theoretical calculations of the \(29\)Si NMR shift for the still elusive \((\text{CH}_3)_3\text{Si}^+\) gave a highly deshielded value of \(\delta^{29}\text{Si} 355.7\). We calculated with the IGLO II method at the level of HF/6-31G* (4) the \(29\)Si shift of 82.1 ppm for the ion (Fig. 1); the result agreed well with the reported experimental shift of 81.8 ppm (5). The \(29\)Si chemical shift of 92.3 ppm in benzene (as opposed to 81.8 ppm in toluene) reflected the weaker \(\pi\)-basicity of the former. When \(\text{m-xylene}\) and \(\text{mesitylene}\) (which are more basic) were used, the \(29\)Si chemical shift became more shielded at 75.9 and 64.5 ppm, respectively, in accord with the expected trend in silylated arenium ions. For Et₃Si⁺ (planar), \(29\)Si was calculated to be 354.6. Lambert et al. (1) suggest that the silyl cation distorts from planarity to relieve external sources of strain and that this leads to the observed large shielding. We have calculated with the IGLO II method at the level of HF/6-31G* the \(29\)Si NMR chemical shift of distorted trimethylsilylenium ion with a C-Si-C angle (a) of 114.00 and 109.47°. We found, however, that they were even more deshielded at 368.2 and 397.0 ppm, respectively, compared to \(\delta^{29}\)Si 355.7 for the planar ion (4). Thus the experimental shift of 81.8 ppm cannot be that of an Et₃Si⁺ species.

Fig. 1. Schema of the \(\rho\)-triethylsilyltoluenium ion. Calculated bond lengths (Å) and bond angles (in parentheses) are Si-C₄, 2.197 (2.18); C₂-C₄, 1.424 (1.40); C₂-C₃, 1.370 (1.37); C₁-C₂, 1.403 (1.38) C₃-C₄-C₅, 117.2 (118); Et₁Si₁, 113.8 (114), Si-C₄-C₁, 110.3, and H-C₄-C₁, 157.9.
Reed et al. recently reported (6) the x-ray structure of the triisopropylsilyl species 1-Pr3Si(14CB11H14), where the brominated carbane Br2CB11H11 was considered to be the least nucleophilic anion now known, indicating the highest degree of silylum ion character (R3Si+) yet observed. Consideration of the x-ray structure (with Si-Br bond distance of 2.479 Å) and the relevant 77Si NMR shift of 109.8 ppm indicate however, that no R3Si+ species was observed, but one in which a single bromine atom was silylated, which resulted in a polarized silyl bromonium zwitterion. Apparently, this zwitterionic complex was so stable that it did not even react with the toluene from which it was isolated. A R3Si+ species with the “highest degree of silylum cation character...yet observed” (6, p. 402) could not display such behavior.

Previously we have called attention (4) to pitfalls with regard to reports of observation, and even of isolation, of “free” long-lived R3Si+ ions or species with a high degree of R3Si+ character that involves “nonnucleophilic” (or “least nucleophilic”) anions and aromatic solvents. Toluene and related π- aromatic hydrocarbons (not unlike n-coordinating solvents such as sulfoxides, ethers, nitriles, ketones, and halogenated systems) are unsuitable for use in obtaining long-lived trivalent tricoordinated silylum cations; they give instead tetracoordinated silylatedonium ions (or zwitterions). Lambert et al. (1) and Reed et al. (6) report significant new results and reliable x-ray structures of isolated silylated ionic complexes. However, both groups incorrectly assign their structures to R3Si+ species (free or closely approaching them). It is not thermodynamic, but kinetic instability in all known condensed phase systems that still renders long-lived trialkysilyl cations elusive.

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Response: We are in essential agreement with Pauling’s calculation and do not believe that it is in contradiction with our own conclusions (1). In our report (contrary to Pauling’s description of it), we were careful to make no claim for a “tricoordinate,” “free,” or “three-bonded” silylvionation. Instead, our title emphasized that there was “distant coordination to solvent” and elsewhere that there was “weakly coordinating toluene” at the fourth coordination site. The unprecedented, long Si-C distance between Et3Si and toluene and the planarity of toluene in an η1 situation indicate that there is only weak coordination between Si and toluene. We attributed the nonplanarity of the triethylsilyl grouping to this interaction. Pauling provides a quantitative expression for what we described as distant or weak coordination. The energetics of this interaction, as we more recently have determined experimentally, are more akin to noncovalent interactions such as H bonds or electrostatic attractions.

We take minor issue only with the bond distance Pauling uses for D(1,0), which he derived from the sum of the Si and C covalent radii of 1.94 Å (2). Actual experimental measurements of C-Si bond lengths in unstrained structures yield a range of about 1.81 to 1.87 Å, with a mean of 1.845 Å from 20 values (3). Long bonds (1.92 to 2.03 Å) have been found only when there are extremely large substituents around Si or C (3), which is not the case for the triethysilylum-toluene system. The longest previously measured Si-C bond length, to our knowledge, is 2.03 Å in the extremely crowded four-membered ring [-(t-Bu)Si(t-Bu)2Si-O-CPh3] (4), hence our use of the descriptor “unprecedented” for the distance between Et3Si and toluene. It is the increase from the normal value of C-Si of about 1.85 Å to the observed value of 2.18 Å that provides the appropriate measure of silylvionation character. If the more likely value for D(1,0) of 1.85 Å is used in Pauling’s equation, then the calculated value of n is 0.28. Thus the structure has 65 to 72% silylum ion character and is properly termed a silylvionation. By the same reasoning, the presence of three normal covalent bonds and one very weak fourth interaction indicates that the structure has more tricoordinate than tetracoordinate character. By contrast, the C-C distance in the σ complex of CH3 to an arene cited by us (1) is 1.56 Å (5). This number is very close to the normal value of 1.54 Å in propane or adamantane (1) and corresponds to a bond order n of 0.93 and to essentially tetracoordination. We thank Pauling for providing this refinement, which enables us to specify more quantitatively the nature of the interaction between Si and toluene in our structure.

The comment by Olah et al. contains (i) a product study, (ii) theoretical calculations of geometries, (iii) theoretical calculations of chemical shifts, and (iv) comments on another recently published report by Reed et al. (6). We shall comment about the first three subjects in turn and shall defer to Reed et al. on the fourth.

The observation of (triethylsilyl)toluene is not relevant to an assessment of the extent of bonding between Si and toluene in the stable ion observed by us in solution and in the solid, as the same product would be expected both from the σ complex (arenium ion) that Olah et al. find in the gas phase by their calculations and from the distantly coordinated system that we observed in the solid. "Inconceivable" notwithstanding, there is firm evidence that these arenes do not react with triethylsilinium in solution. Reed et al. (6) recrystallize their compounds from toluene without reaction. Both Olah and Reed maintain that the carbane ion is less nucleophilic than our borate. It does not follow then that the supposedly more closely bound (to anion) Si ion in our case is more likely to react with toluene. We have observed that toluene and other solvents exchange rapidly on the NMR time scale between bound and unbound states with the silyl cation (7). Thus triethlysilylum exhibits only one 29Si peak in a mixture of benzene and toluene, with a chemical shift intermediate between those in the pure solvents. A "reaction" as envisaged by Olah et al. would have led to two distinct σ complexes. In the system methyl-diisopropylsilanyl tetrakis(pentafluorophenyl)borate, the isopropyl methyls are homotopic in the 1H and 13C spectra, again indicative of fast exchange. If the exchange of solvent on Si is dissociative rather than associative, as argued by both Boudjouk (8) and Tilley (9), an upper limit of about 15 kcal mol−1 may be placed on the barrier to dissociation of Si from toluene, for the given temperature and chemical shift difference. Such an observation does not support a "reaction," but again is more akin to the energetics of H bonds or electrostatic interactions.

With regard to theoretical calculations of geometry, there are appreciable and systematic differences between the gas phase geometry calculated by Olah et al. and the observed geometry in the solid. The calculations by Schleyer et al. (10) were at a higher level (MP2(fc)/6-31G* for the H3Si+ structure), but suffered from a similar
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