Triethylsilyl Cations

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

(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}Si\textsuperscript{+}((C\textsubscript{6}H\textsubscript{5})\textsubscript{4}B(C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3})\textsubscript{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 C\textsubscript{4} 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)

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

different distances lead to \( n = 0.35 \) for the bond number.

Lambert et al. state that the observed Si-C bond length to C\textsubscript{4} 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(C\textsubscript{2}H\textsubscript{5})\textsubscript{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\textsubscript{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 trimethylsilylenium 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 σ-bonding interaction, and that the observed nonplanarity of the free trimethylsilylenium ion results from weak interaction with toluene, which causes distortion. However, if the trimethylsilylenium ion could exist as a long-lived species, it is inconceivable that it could not react with toluene (a good π-base). To probe this question, we repeated the work of Lambert et al. and obtained their reported ionic complex. When the complex was quenched with a hindered base besides hexaethylsiloxane, we then obtained triethylsilyltoluenes, albeit in low (7%) yield. This result is in accord with the formation of the intermediate trimethylsilyltoluene ion which, on competing deprotonation with desilylation, gives the silylated toluenes. Subsequently, we have fully optimized the geometry of the \( \rho \)-trimethylsilyltoluene 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 tol-