Communications to the Editor

An ab Initio Molecular Orbital Calculation of the Structure of Silabenzeno

Sir:

Silabenzeno has proven to be an elusive molecule despite the relative stability of similar heteroatomic analogues of benzene such as pyridine, phosphabenzene, arsabenzene, and stibabenzene. Attempts have been made to generate a substituted silabenzeno with the following rearrangement of a singlet carbenon.

\[
\begin{array}{c}
\text{H} & \text{C} & \text{Si} \\
\end{array}
\]

Although this reaction occurs readily for carbon, the silicon analogue does not appear to yield a silabenzeno. In this communication we wish to report an ab initio investigation of the structure of silabenzeno.

The calculations were performed with the GAUSSIAN 70 and the FORCE programs using the standard STO-3G basis set on the IBM 360/91 computer at Princeton. The force method was used to optimize fully all geometrical parameters in the structures reported. Because of difficulties associated with choosing a suitable, nonredundant internal coordinate system for cyclic molecules, the optimization was based on cartesian energy derivatives. An initial force constant matrix was obtained by transforming a simple, empirical valence force field using redundant internal coordinates to the cartesian coordinates system. (The accuracy of the initial force constant matrix affects only the rate of convergence, not the final outcome of the geometry optimization. The force method, especially when combined with an empirically estimated force constant matrix, can be an order of magnitude more efficient than optimization methods based only on the energy. In addition, magnitudes of the residual forces at the optimized geometry provide an important check on the quality of the optimization. The force method, especially when combined with an empirically estimated force constant matrix, can be an order of magnitude more efficient than optimization methods based only on the energy. In addition, magnitudes of the residual forces at the optimized geometry provide an important check on the quality of the optimization.)

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Inspection of the geometrical parameters for singlet silabenzeno reveals that only small changes in the bond angles (relative to benzene) are necessary to accommodate the larger silicon. The C–C bond lengths are essentially the same as in benzene, and the Si–C bond length lies between the values for a single bond and a double bond, displaying almost the same relative shortening found in benzene. Thus, the calculated structures would suggest that silabenzeno possesses some degree of aromaticity. In the triplet state, these bond lengths increase somewhat; but, unlike silaethylene, where the triplet undergoes a large conformational change, triplet silabenzeno remains planar.

Further support for the aromatic character can be found in the molecular orbital (MO) energies and MO coefficients. The usual benzenoid pattern of orbital energies (~0.461, 2 × (~0.283), 2 × (~0.271), 0.507 au calculated for CsH6 at STO-3G) is not strongly perturbed (~0.416, ~0.278, ~0.200, 0.256, 0.284, and 0.494 au), although the energy of the highest occupied MO is above that of benzene, suggesting less resonance.
that silabenzene may have considerable ylide character, al-
or strong geometrical distortion.

The Mulliken population analysis in Table II shows that the σ-electron distribution is reasonably uniform, with the silicon having a somewhat smaller electron density than the carbons. Correspondingly, there is a charge buildup on the ortho and para carbons typical of a benzenoid σ system. The σ framework shows a more distinct polarization of the C–Si bond than does the σ-electron system. This suggests that silabenzene may have considerable ylide character, although this effect may be exaggerated by deficiencies inherent in the Mulliken population analysis. The elusive character of silabenzene may thus be due to its high reactivity as opposed to a lack of aromaticity.

In considerable error in estimated heats of isomerization, the calculated energy differences for eq 2 are sufficiently large so that trends should be predicted correctly. The formation of silabenzene in rearrangement 2a of the singlet carbene is calculated to be 31 kcal/mol less exothermic than the formation of benzene. For triplet reaction 2b, the isomerization is thermodynamically favored to proceed in the opposite direction.

The difference in isomerization energies in reaction 2a might suggest a lack of resonance stabilization in silabenzene. However, this would contradict the interpretation of the calculated structure. The problem can be resolved by comparison with a simpler carbene rearrangement:

\[ X = \text{Si} \quad \text{C} \quad \text{Si} \quad X = \text{C} \]

The triplet isomerizations are nearly thermoneutral. However, the formation of singlet silaethylene is calculated to be 21 kcal/mol less exothermic than the formation of ethylene, partially as a result of the lower strength of the Si–C σ bond compared with the C–C σ bond. The same effect is present in eq 2a and accounts for a large portion of the isomerization energy difference, with the remainder (10 kcal/mol) attributable to resonance energy differences. In fact eq 2a and 3a can be combined for an estimate of the resonance energy of silabenzene:

\[ \text{X} = \text{Si} \quad (22 \text{ kcal/mol}) \]
\[ \text{X} = \text{C} \quad (32 \text{ kcal/mol}) \]

The value for benzene is in fair agreement with experiment and the calculated resonance energy of silabenzene is \( \frac{1}{3} \) that of benzene. Even though other isomers of CsSiHs such as Dewar silabenzene and 1-silacyclohexadienylidene (cf. silaethylene vs. methylsilene) may be competitive in stability, silabenzene appears to have all the attributes expected of an analogue of benzene.

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References and Notes


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The Significance of a Secondary Deuterium Isotope Effect in the Photorearrangement of 1-Iminopyridinium Ylides

Sir:

In photoreactions which appear to involve a thermally activated step, a comparison of the temperature dependence of the luminescence with the quantum yield is the current method of choice in characterizing the mechanistic pathway. For instance, in the singlet process of eq 1, which converts X to Z via

\[
\begin{array}{c}
\text{X} \\
\xrightarrow{h_\nu} \\
\text{X}^* \\
\xrightarrow{h_\nu} \\
\text{Y} \\
\xrightarrow{h_\nu} \\
\text{Z}
\end{array}
\]  

(1)

the intermediate Y, the temperature dependence of the fluorescence yield is independent of the rate ratio \(a/b\), but a direct, concerted, transition of \(X^*\) to \(Z\), which did not involve the intermediate \(Y\) and its thermal conversion to \(Z\), requires that quantum yield be inversely related to the fluorescence rate. An alternative approach to the problem of proving the occurrence of a thermal reaction step in the course of a photoreaction, through measurement of a kinetic isotope effect for the proposed vibrationally activated process, promises to be somewhat simpler to apply, and is the subject of this report.

Streith and Cassal have discussed the reversible conversion of 1 to 2 taking place readily upon exposure of a solution to UV radiation. The reverse reaction has now been effected by purely thermal means. This permits an operational assumption similar to one made by Ullman that the same reaction transition state can be attained from either direction, and that the forward reaction brought about by photochemical means is comprised of an initial absorption and electronic transition to an excited singlet state. The latter crosses to a high vibrational level of the ground state, subsequently achieving the vibrational energy required to surmount a thermal reaction barrier. The kinetic isotope effect experiments of moment have been devised and carried out in the interests of providing a broad test of the validity of this assumption. In point of fact, however, these isotope effects in this reaction arising from differences in extinction coefficients of competing isotopic substrates since the competing isotopic reaction sites are in the same molecule. The relative rates at the isotopically substituted centers depend on the localization of the absorbed energy in the critical bonds, a process which is affected only by the vibrational frequencies of \(H\) and \(D\) nuclei bonded to identical carbon atoms. Moreover, since these \(H\) and \(D\) nuclei are not directly involved in the course of rearrangement, the Hammond theory would predict that the deuterated carbon should be less reactive, if at all different from its protiated competitor in this respect.

The 2-deuterio-1-iminopyridinium ylide substrate 1a was synthesized in the usual manner from 2-deuteriopyridine. This precursor, in turn, was made by a preceding procedure involving exchange of 2-pyridinecarboxylic acid with \(D_2O\) followed by thermolytic decarboxylation to give a product with the required degree of 2-deuteration. The photorearrangement of 1a was carried out in all other respects exactly as in the previous studies. Samples taken at various extents of reaction completion showed, to all purposes, identical compositions of products 2a and 2b (See Table I).

Clearly the finding of a very large, inverse, secondary deuterium isotope effect in the photorearrangement of 1-imino-