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ON THE INVERSION BARRIERS IN THE DI- AND TRI-BENZOSILEPINS

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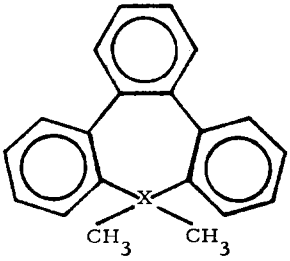
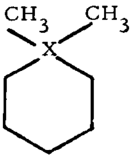
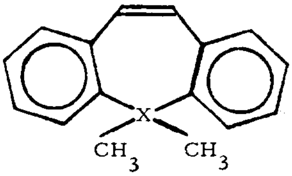
The barrier to the inversion of the 9,9-dimethyl-9H-tribenzo[b, d, f]silepin (I) molecule was recently studied and discussed[1] in comparison with the barrier for the corresponding hydrocarbon (II). In general it is found that rotational barriers are lower in the silanes than they are in the corresponding hydrocarbons, and it has been suggested that this is due largely to the longer Si–C bond[2]. Thus it is anticipated and found that the barrier to rotation in methylsilane is lower than that in ethane. The inversion barrier in 1,1-dimethylsilacyclohexane (III) is approximately half[2] that which is found for 1,1-dimethylcyclohexane (IV). The paper by Corey and Corey[1] pointed out that the inversion barrier in I was similar to or higher than that found for II (only a minimum value was found for the barrier of I). No explanation was offered for this seemingly unexpected state of affairs.



I X = Si
II X = C



III X = Si
IV X = C



V X = Si
VI X = C

Some time ago we described a molecular mechanics method for the calculation of geometries and energies of alkanes and related compounds[3]. The method was subsequently extended to include silanes[4]. It has also been applied to molecules containing delocalized electronic systems[5], and specifically it has been applied in detail to cyclooctatetraene and many of its derivatives[6]. The calculational methods and parameters are substantially the same as those described earlier.

For structures I and II, the barrier height was calculated by first calculating the energy of the relaxed state, in which the seven membered ring was invariably in a tub form. The transition state was then constrained to have the seven membered ring, the attached aromatic rings, and all their attached hydrogens coplanar, but it was otherwise allowed to relax in all degrees of freedom. The exact transition state geometry is not known, and it may be that it is not completely coplanar. However, while this would lead to errors in the absolute energies calculated, it would lead to relatively little error when differences in barrier heights between I and II are compared. The results obtained are given in Table I.

TABLE I

Inversion Barriers for Silane Heterocycles and Carbocyclic Analogs

Compound	$\Delta G^{\ddagger}$(kcal/mole) Observed	$\Delta G^{\ddagger}$(kcal/mole) Calculated
I	23.5[a]	45.4
II	24.0[7]	33.9
V	10.8[a]	8.5
VI	9.1[7]	7.3

[a] The minimum barrier height for I was calculated using the coalescence formula[8] and data from ref. 1. The maximum barrier height for V was calculated using the coalescence formula and data from ref. 9, assuming a maximum shift difference of 1Hz. Use of a larger shift difference would result in a smaller barrier.

The calculations indicate that the inversion barrier in I should indeed be appreciably larger than that in II. An examination of the calculated values shows clearly why this is true. Because the C–Si bond length is considerably longer than the C–C bond length, the heptagonal ring in the heterocyclic compound is irregular, in such a way as to force together the o-hydrogens on benzene rings adjacent to the seven membered ring. This leads to an increase in the transition state energy in the planar silicon compound, relative to the carbon compound, without any corresponding increase in the ground state energies, and hence to an increase in the inversion barrier. The change in the distance between the o-hydrogens in the planar form of I vs. II is not very great (1.94 vs. 1.99Å), but that is the resulting change in distance after the molecules have relaxed, and considerable bending energy has also been introduced.

We also studied the corresponding dibenzo compounds, where the benzene ring furthest from the silicon has been removed, and replaced by a double bond. In this case the vinyl hydrogens are much further from the o-hydrogens, 2.26 vs. 2.31Å in the silicon and carbon compounds respectively. The barriers are therefore much lower, and the differences much less. Because of the very hard characteristics of the Van der Waals repulsion curve, a similar distance difference corresponds to a much lower energy difference as the Van der Waals minimum is approached. The calculated and experimental values seem to be in reasonable agreement for all of these compounds.

It is concluded that the larger barrier in I with respect to II is in no way anomalous, but is simply a result of the differences in the bond lengths of C–C and C–Si bonds, and the geometric differences which then follow.

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