evaporate, giving **12** as well-defined needles, mp 90 °C: ^{1}H NMR ($CDCl_3$) δ 1.42 (ss, 6 H, acetonide CH_3), 3.7 (m, 2 H, CH_2OBzl), 4.1 (m, 2 H, OCHCHO), 4.62 (s, 2 H, CH_2Ph), 4.98 (br s, 1 H, C*H*NH), 5.3 (m, 2 H, C=CH_2), 6.0 (m, 1 H, C*H*=CH_2), 6.84 (d, 1 H, NH), 7.4 (sd, 7 H, Ph and 3,5-Ar), 7.74 (d, 2 H, 2,6-Ar); $[\alpha]^{26}{}_D$ +19.2° (*c* 0.5, acetone); MS (FAB) *m/e* 416 (18, M + 1), 358 (100). X-ray crystallographic data[14] for $C_{23}H_{26}ClNO_4$ (415.92): orthorhombic, space group $P2_12_12_1$, a = 8.443, b = 49.540, and c = 5.203 Å, V = 2176.2 Å^3, Z = 4, D_{calc} = 1.269 g cm^{-3}.

[2*S*-(2α,3β,4β)]-2-(Acetylamino)-2,3-dihydro-3-hydroxy-4-(hydroxymethyl)-2(5*H*)-furanone (*N*-Acetylpolyoxaminolactone)[1a] (20). A suspension of 200 mg of **2b** in 20 mL of MeOH was treated with 1 mL of acetic anhydride and stirred vigorously for 18 h as described previously.[1a] After addition of water, the solution was evaporated and the residue was chromatographed (silica gel, MeOH–EtOAc). The residue obtained was triturated with CH_3CN to leave a white powder, which was crystallized from a small volume of EtOH to give **20**, mp 146–150 °C (lit.[1a] mp 150–152 °C): ^{1}H NMR ($CDCl_3$–trace Me_2SO-d_6) δ 2.26 (s, 3 H, CH_3), 3.9 (m, 3 H, C*H*(OH)C*H*(CH_2OH) and 1° OH), 4.6 (m, 3 H, CH_2 and CHN), 5.33 (d, 1 H, 2° OH), 7.50 (br s, 1 H, NH); MS (FAB), *m/e* 215 (100, M + Na), 190 (17, M + 1). X-ray crystallographic data[14] for $C_7H_{11}NO_5$ (189.17): orthorhombic, space group $P2_12_12_1$, a = 12.182, b = 13.872, and c = 4.977 Å, V = 841.1 Å^3, Z = 4, D_{calc} = 1.494 g cm^{-3}.

Acknowledgment. We gratefully acknowledge the assistance of the Physical Analytical Department of Schering-Plough Corp.

Supplementary Material Available: Views of the solid-state conformations of **12** and **20**, tables of crystal data, atomic postional and thermal parameters, bond distances and angles (8 pages). Ordering information is given on current masthead page.

Pyramidal Inversion and Electron Delocalization in the Silacyclopentadienyl Anion

James R. Damewood, Jr.

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received September 2, 1986

Despite growing interest in the chemistry of silicon derivatives of aromatic hydrocarbons,[1] relatively little information is available on the geometric and electronic structure of these compounds. We now report the results of ab initio calculations on the silacyclopentadienyl anion (1)[2,3] (the monosilicon derivative of the cyclopentadienyl anion) that reveal a rigidly pyramidal ground-state structure and an extremely low resonance energy for this compound.

Calculations were performed on the planar (C_{2v}) and pyramidal (C_s) forms of 1 at the 6-31G* level of sophistication using the program Gaussian 82.[4] Complete geometry optimizations were performed on these structures under C_{2v} and C_s symmetry constraints. Selected structural parameters[5] obtained for these two conformations are reported in Figure 1. We find that the ground-state conformation of 1 is the pyramidal C_s structure (Figure 2). The planar, C_{2v} form is found to be the transition state for pyramidal inversion between equivalent C_s structures. We calculate an inversion barrier ($C_s \rightarrow C_{2v}$) for this process of 16.2 kcal/mol.[6] The structural parameters that we obtain for the C_{2v} form of 1 compare well with those obtained previously by Gordon et al.[2] at the STO-2G level of sophistication. While only the C_{2v} conformation was considered in this previous study,[2] its properties are of particular interest since favorable orbital alignment would be expected to result in electron delocalization being at a maximum in this planar conformation (see below). Inspection of Figure 1 reveals that the structure of the ground-state C_s conformation differs significantly from that found for the planar form. In this structure the geometry about silicon is markedly pyramidal with a 68.2° angle between the Si-H bond and the mean plane of the ring heavy atoms.[7] While less pronounced, this pyramidality extends to all of the heavy atom centers in the C_s conformation.[8] Also noteworthy is the much longer Si-C bond (1.924 Å) in this conformation compared to that obtained for the C_{2v} form (1.788 Å). Concomitant with this increase in Si-C bond lengths is a decrease in the C–Si–C angle from 96.7° (C_{2v}) to 86.5° (C_s) and an increase in the Si–C–C angle from 104.8° (C_{2v}) to 110.4° (C_s). In addition, while the C–C bond lengths in the C_{2v} transition state are closely similar (1.401 and 1.405 Å), in the C_s ground state these bond lengths differ significantly (1.341 and 1.472 Å) and suggest that the hydrocarbon portion of the molecule may best be described as adopting substantial butadiene-like (localized) character. Qualitatively this structural feature, along with the lengthening of the Si-C bond, suggest that electron delocalization is significantly reduced in the C_s conformation relative to the C_{2v} form.

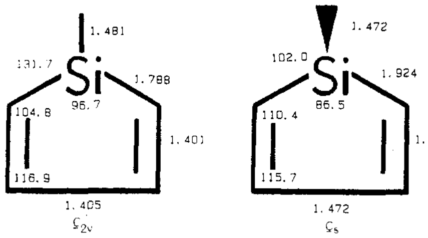


Figure 1. Calculated bonding parameters for conformations of 1 (bond lengths in Å, bond angles in degrees). Left: C_{2v} conformation. Right: C_s conformation.

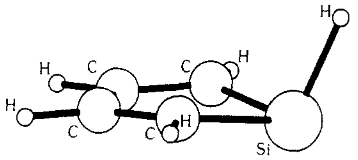


Figure 2. View of the calculated ground-state structure (C_s) for 1.

---

[1] See: Clabo, D. A., Jr.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 1664, reference 2, and references therein. See also: Gordon, M. S. In *Molecular Structure and Energy*; Liebman, J., Greenberg, A., Eds.; VCH Publishers: Dearfield Beach, FL, Vol. 1, in press.

[2] Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972. In this work the C_{2v} form of 1 was investigated at the 3-21G//STO-2G level of sophistication.

[3] Portions of this work were presented at the 20th Organosilicon Symposium, April 18–19, 1986.

[4] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, M. J.; Pople, J. A. A copy of the program may be obtained from Carnegie-Mellon University.

[5] For C_{2v}, C–H = 1.077 (1.082) Å; for C_s, C–H = 1.082 (1.085) Å; α-C (β-C).

[6] Total energies in hartrees/molecule (6-31G*) are : C_s, −443.22440; C_{2v}, −443.19853.

[7] Structural parameters were calculated by using the program *Geom*.

[8] Pyramidality at all heavy atom centers is expected under C_s symmetry.

0022-3263/86/1951-5028$01.50/0

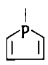
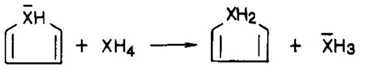


Figure 3. The phosphole nucleus.

In order to quantitatively assess the extent of electron delocalization in the ground state of 1 and to compare it to the cyclopentadienyl anion, we calculated energy differences for the isodesmic[9] reaction shown in eq 1 (X = C or Si). The energy difference of 73.4 kcal/mol obtained for this reaction when X = C[10] provides an estimate of the resonance energy for the cyclopentadienyl anion. This value is in reasonable agreement with the resonance energy estimate obtained by Gordon et al.[2] at the 3-21G//STO-2G level of sophistication. For X = Si, the C_s conformation provides an energy difference of only 2.2 kcal/mol.[12] This value is substantially smaller than the previous estimate[2] of the resonance energy of 1 (23 kcal/mol) which was based on the C_{2v}, planar structure. Since pyramidalization at silicon should decrease the efficiency of silicon–carbon (p–p) π overlap[13] and hence the extent of electron delocalization, these findings are in complete accord with our qualitative expectations. The present calculations thus substantially lower the current estimate of the resonance energy for 1. On the basis of these calculations we conclude that the ground state of 1 has only ca. 3% of the resonance stabilization exhibited by its carbon analogue, the cyclopentadienyl anion.



(1)

An interesting comparison may be made between 1 and the isoelectronic phospholes (Figure 3). The barrier to pyramidal inversion in phosphine is calculated to be at least 37 kcal/mol.[14] In simple phospholes the barrier to pyramidal inversion at phosphorus is substantially decreased from this value to ca. 16 kcal/mol.[15] Structurally, however, the pyramidality at phosphorus is not significantly altered in these compounds relative to that found for phosphine.[16] Similarly, we find that the inversion barrier in 1 (16.2 kcal/mol) is significantly reduced relative to the ca. 26 kcal/mol obtained[17] for the silyl anion. Further, using the sum of the angles about silicon as a measure of pyramidality, the C_s conformation (290.5°) does not differ significantly from the silyl anion itself (291.1°,[17] 292.8°[18]). Evidently, as for the phosphines,[15,16] substituents that lower the barrier to pyramidal inversion at silicon in the silyl anions do not necessarily cause a flattening of the silicon pyramid.[19]

The inversion barrier and resonance energy calculated in the present work lead to a number of interesting predictions regarding the static and dynamic stereochemistry of 1 and its closely related derivatives. For example, while attempts to measure the inversion barrier in a silyl anion[20] have long been thwarted by barriers that exceed the limits of dynamic NMR (DNMR) methods (i.e., >24 kcal/mol),[20] the present calculations suggest that investigations of suitable derivatives of 1 would be a promising direction for future experimental efforts in this area. In addition, the current level of interest in generating η^5 metal complexes of derivatives of 1[21] calls for detailed understanding of the electronic structure of the silacyclopentadienyl anion fragment.[2] On the basis of our relatively localized picture of electron distribution in the π system of 1, one would predict that the stability of these η^5 metal complexes will be significantly lower than that found for their all-carbon analogues.

Acknowledgment is made to IBM Corporation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Thanks go to Prof. M. Gordon for helpful discussions.

Registry No. 1, 85883-41-6; cyclopentadienyl, 12127-83-2.

---

[9] For example, see: Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

[10] All structures were completely optimized for parent symmetries. Total energies in hartrees/molecule (6-31G*) are: C_5H_6, −192.79172 (C_{2v}), C–H(CH_2) = 1.089 Å, C_α–H = 1.073 Å, C_β–H = 1.074 Å, CH_2–C_α = 1.506 Å, C_α–C_β = 1.328 Å, C_β–C_β = 1.477 Å, C_α–CH_2–C_α = 102.5°, CH_2–C_α–C_β = 109.6°, C_α–C_β–C_β = 109.2°, CH_2–C_α–H = 123.7°, H–C–H = 106.7°, C_α–C_β–H = 126.4°, C_α–CH_2–H = 111.9°; CH_3^-, −39.46684 (C_{3v}, obtained from CMU data base[4]). $C_5H_5^-$, −192.180412 (D_{5h}) C–H = 1.080 Å, C–C = 1.402 Å; CH_4, −40.19517 (T_d, obtained from CMU data base[4]). Experimentally the resonance energy for the cyclopentadienyl anion is estimated at 24–27 kcal/mol.[11] This suggests that any systematic error in our calculations will lead to an overestimation of the resonance energies.

[11] Bordwell, F. G.; Drucher, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632.

[12] Total energies in hartrees/molecule (6-31G*) are: C_4H_6Si, −443.83985 (C_s); SiH_3^-, −290.60611 (C_{3v}); $C_4H_5Si^-$ −443.22440 (C_s); SiH_4, −291.22513 (T_d).

[13] See, for example: Damewood, J. R., Jr.; Mislow, K. *Monatsh. Chem.* **1980**, *111*, 213 and references therein.

[14] Lehn, J. M.; Munsch. B. *Chem. Commun.* **1969**, 1327; *Mol. Phys.* **1972**, *91*, 23. See also: Boggs, J. E. *J. Chem. Phys.* **1977**, *66*, 5769 and references therein.

[15] Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6205. Rauk, A.; Andose, J. D; Frick, W. G.; Tang, R. Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507.

[16] Mislow, K. *Trans. N. Y. Acad. Sci.* **1973**, *35*, 227.

[17] Eades, R. A.; Dixon, D. A. *J. Chem. Phys.* **1980**, *72*, 3309 and references therein.

[18] Keil, F.; Ahlrichs, R. *Chem. Phys.* **1975**, *8*, 384.

[19] However, the silylborane anion is calculated to be planar. Hopkinson, A. C.: Lien, M. H. *Tetrahedron* **1981**, *37*, 1105.

[20] Lambert, J. B.; Urdaneta-Pêrez, M. *J. Am. Chem. Soc.* **1978**, *100*, 157 and references therein.

[21] Carrê, F.; Colomer, E.; Corey, J. Y.; Corriu, R. J. P.; Guêrin, C.; Henner, B. J. L.; Kolani, B.; Man, W. W. C. W. C. *Organometallics* **1986**, *5*, 910.

Correlation of the Rates of Solvolysis of the Methyldiphenylsulfonium Ion[1]

Dennis N. Kevill* and Steven W. Anderson

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received July 21, 1986

In conjunction with the development[2,3] (eq 1) of a scale of solvent nucleophilicities ($N_{\mathrm{Et_3O^+}}$) based upon the specific rates of solvolysis of the triethyloxonium ion in a given solvent (k) and in the standard (80% ethanol) solvent (k_0),

$$\log (k/k_0) = N_{\mathrm{Et_3O^+}} \qquad (1)$$

we tested the utility of the scale in the correlation of the rates of solvolysis of other RX^+ substrates. A measure of the sensitivity (l) of the specific rates of solvolysis of RX^+ substrates towards changes in solvent nucleophilicity can be obtained from eq 2.

$$\log (k/k_0)_{RX^+} = lN_{\mathrm{Et_3O^+}} \qquad (2)$$

Obvious candidates for study are the structurally related trisubstituted sulfonium ions. These react, however, much

---

[1] Abstracted, in part, from the Ph.D. Dissertation of S.W.A., Northern Illinois University, Aug 1985.

[2] Kevill, D. N.; Lin, G. M. L. *J. Am. Chem. Soc.* **1979**, *101*, 3916.

[3] Kevill, D. N.; Anderson, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 1579.