Journal of Organometallic Chemistry, 166 (1979) 21—24

A THEORETICAL STUDY OF SILABENZENE

PETER H. BLUSTIN
Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)
(Received July 31st, 1978)

Summary

Calculations on the structure and properties of silabenzene suggest that the main obstacle to the formation of the molecule may be thermodynamic.

Introduction

The participation of heteroatoms in planar condensed hydrocarbons exhibiting aromatic properties is a well-known phenomenon. Silicon, although a member of Group IVb, does not form stable multiply-bonded compounds [1] and it has never been observed substituted for carbon in a stable heteroaromatic system [2], although methyl-silabenzene has been postulated as an as yet non-isolated intermediate [3]. The purpose of the present study is to investigate the electronic structure of silabenzene and to compare its properties with those of benzene, the prototypical aromatic molecule.

The method used is an adaption of Frost's Floating Spherical Gaussian Orbital (FSGO) model [4]. No previous ab initio calculations on silabenzene have appeared in the literature.

Calculations

The description of the silicon *KL* shells is as employed previously [5]. The π-electron system is described by two-bond (or three centre) two-electron localised orbitals [6], as illustrated in Fig. 1. All σ- and π-orbitals were constrained to move along bond axes and, in addition, orbitals between carbon centres were fixed at the midpoint of the bond. This approach, when used for benzene, produces the full D_{6h} symmetry (within 0.04%) starting from D_{3h}. The calculation for silabenzene used orbital exponents and multipliers taken from the earlier benzene calculation [6] for the carbon core, C—H, σ(CC) and π(CC) orbitals. Otherwise, all geometrical and orbital parameters were optimised to give the lowest variational energy for the $^1A_1$ state.

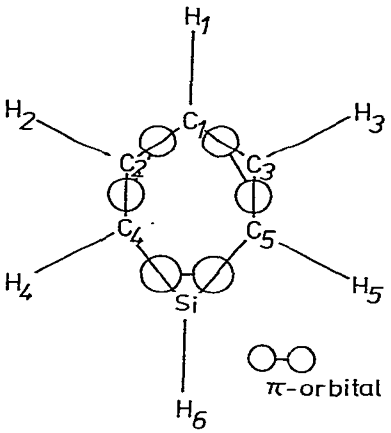

Fig. 1. FSGO description of silabenzene. The π-orbitals are represented by the sum of adjacent *p*-orbitals situated along the C—C or C—Si bonds.

Results

The structure obtained for silabenzene is compared with theoretical [6] and experimental [7] results for benzene and the latest gas phase geometries of pyridine [8] and phosphorin [9] in Table 1. The alternation in C—C bond lengths between the heteroatom and C(1) is a common feature of heteroaromatic systems. For silabenzene and phosphorin the C—C distance increases on the average over the benzene value whereas a decrease is observed for pyridine. The origin of this effect is electronic in nature rather than due to the size of the substituent atom. The central C—Si—C angle is close to tetrahedral, as

TABLE 1

GEOMETRIES OF BENZENE, SILABENZENE, PYRIDINE AND PHOSPHORIN

	Benzene [4] [a]	Silabenzene	Pyridine [6]	Phosphorin [7]
Bond lengths (Å)				
r(C(1)C(2))	1.411	1.420	1.3916	1.384
r(C(2)C(4))	1.411	1.409	1.3938	1.413
r(C(4)X)	1.411	1.819	1.3376	1.733
r(C(1)H(1))	1.094	1.099	1.0818	1.122
r(C(2)H(2))	1.094	1.088	1.0826	1.122
r(C(4)H(4))	1.094	1.097	1.0865	1.122
r(XH(6))	1.094	1.446	—	—
Bond angles (degrees)				
C(2)C(1)C(3)	120	126.9	118.40	122.7
C(1)C(2)C(4)	120	122.7	118.53	123.7
C(2)C(4)X	120	122.5	123.80	124.4
C(4)XC(5)	120	102.7	116.94	101.1
XC(4)H(4)	120	123.0	116.01	(117.8)
C(4)C(2)H(2)	120	120.4	120.12	(118.2)

[a] Experimental *r*(CC) 1.397 Å, *r*(CH) 1.084 Å.

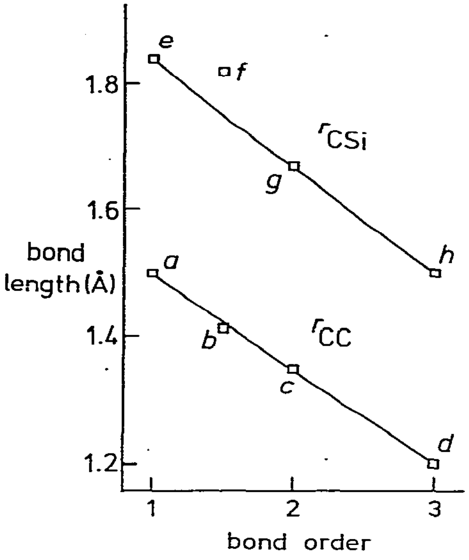

Fig. 2. Graph of bond order versus bond length for (a) ethane, (b) benzene, (c) ethylene, (d) acetylene, (r(CC)) and (e) silylmethane, (f) silabenzene, (g) silaethylene, (h) silaacetylene (r(CSi)).

predicted for the H—Si—H angle in $CH_2{=}SiH_2$ [5].

Figure 2 plots the calculated C—C (for ethane [5], benzene [6], ethylene and acetylene [5]) and C—Si (for silylmethane, silabenzene, silaethylene and silaacetylene [5]) bond lengths versus the expected bond order (number of electrons per bond, divided by two). Whilst r(CC)(benzene) lies close to the r(CC)-bond order curve, r(CSi)(silabenzene) is situated well above the corresponding r(CSi) curve. This indicates that the C—Si bond order in silabenzene is only just above one (lateral displacement of r(CSi)(silabenzene) to the r(CSi)-bond order curve gives just over 1.1, compared with 1.6 for benzene after a similar displacement).

Atomisation of benzene breaks six C—H and six C$\overset{\cdots}{-}$C bonds. Using standard values for ΔH_f^0[C(g)] and ΔH_f^0[H(g)] together with $\Delta H_f^0[C_6H_6(g)]$ we obtain B(C$\overset{\cdots}{-}$C) 508 kJ mol^{-1} if B(C—H) 413 kJ mol^{-1} [5]. Atomisation of silabenzene breaks four C$\overset{\cdots}{-}$C, two C$\overset{\cdots}{-}$Si, one Si—H and five C—H bonds. The two molecular atomisations may be calculated theoretically, using E[C(g)] −31.665250 a.u., E[Si(g)] −247.912092 a.u., E[H(g)] −0.424413 a.u. [10], $E[C_6H_6(g)]$ −195.017333 a.u. [6] and $E[C_5SiH_6(g)]$ −411.041967 a.u., and the relationship B(C$\overset{\cdots}{-}$C) = B(C$\overset{\cdots}{-}$Si) + 245 kJ mol^{-1} obtained. This produces B(C$\overset{\cdots}{-}$Si) 263 kJ mol^{-1}, which is intermediate between values calculated for B(C—Si) 234 kJ mol^{-1} and B(C=Si) 327 kJ mol^{-1} [5], and is in proportion to the above estimate of the C$\overset{\cdots}{-}$Si bond order.

The calculated dipole moment for silabenzene is 2.85 D, polarised such that the positive end of the dipole vector points toward silicon. Using standard values for $\mu(C^-H^+)$ (0.4 D) and $\mu(Si^+H^-)$ (1.0 D) [5] we find $\mu(C^-\overset{\cdots}{-}Si^+)$ 2.87 D. This is bracketed by $\mu(C^-{-}Si^+)$ 0.95 D and $\mu(C^-{=}Si^+)$ 3.94 D ("d_π" calculations [5]).

A population analysis [11] of the silabenzene wavefunction in the C—Si—C

TABLE 2

POPULATION ANALYSIS OF C—Si—C GROUPING IN SILABENZENE

	N(Si)		N(C)
KL	10	*K*	2
SiH	0.6330	CH	0.7558
σ(SiC)	1.2246	σ(CC)	1
π(SiC)	1.9755	σ(SiC)	1.3877
Total	13.8331	π(CC)	1
Z_{net}	+0.1669	π(SiC)	0.0122
		Total	6.1557
		Z_{net}	—0.1557

bonds is given in Table 2. The electronic effect of silicon substitution in the benzene ring is to draw π-electrons to the larger atom, which in turn loses more σ-electrons to the adjacent carbon centres. This movement of charge parallels that in the borazine molecule [6], which has $-I_\sigma$(N) and $+I_\pi$(B) and also $I_\sigma > I_\pi$.

Discussion

To sum up, the introduction of silicon into an aromatic system is to (a) produce a smaller-than-tetrahedral C—Si—C angle in the ring and (b) a relatively long $\mathrm{C\overset{\cdots}{-}Si}$ bond of low bond order, low π-bond energy ($D_\pi \sim 29$ kJ mol^{-1}, to be compared with $D_\pi(\mathrm{C\overset{\cdots}{-}C}) \sim 161$ kJ mol^{-1}) and high polarity. The disposition of electron population indicates that the molecule is open to nucleophilic attack at the silicon centre and that therefore strong nucleophiles should be excluded in the final steps of possible schemes to prepare silabenzene [2]. Conversely, the large silicon (diffuse) p-electron population (Table 2) implies that the silicon centre may also be attractive to electrophiles. Nevertheless, the largest obstacle to the formation of silabenzene is thermodynamic. If only 58 kJ mol^{-1}, twice $D_\pi(\mathrm{C\overset{\cdots}{-}Si})$, may be obtained following the loss of one tetrahedral bond to silicon (the lowest in value is probably B(Si—Si) 226 kJ mol^{-1} [12]), then there should be considerable gains in energy terms (>168 kJ mol^{-1} if an Si—Si bond is broken) to be made from the other parts of the molecular precursor.

References

1 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, Accounts Chem. Res., 8 (1975) 18.
2 P. Jutzi, Angew. Chem. Int. Ed. Engl., 14 (1975) 232.
3 T.J. Barton and D.S. Banasiak, J. Amer. Chem. Soc., 99 (1977) 5199.
4 A.A. Frost, J. Chem. Phys., 47 (1967) 3707, 3714.
5 P.H. Blustin, J. Organometal. Chem., 105 (1976) 161.
6 P.H. Blustin, Mol. Phys., 36 (1978) 279.
7 A. Langseth and B.P. Stoicheff, Can. J. Phys., 34 (1956) 350.
8 F. Mata, M.J. Quintana and G.O. Sorensen, J. Mol. Struct., 42 (1977) 1.
9 T.C. Wong and L.S. Bartell, J. Chem. Phys., 61 (1974) 2840.
10 P.H. Blustin and C.G. Whittaker, unpublished results.
11 G. Simons and E.R. Talaty, Chem. Phys. Lett., 38 (1976) 422.
12 D.A. Johnson, Some Thermodynamic Aspects of Inorganic Chemistry, Cambridge University Press, London, 1968.