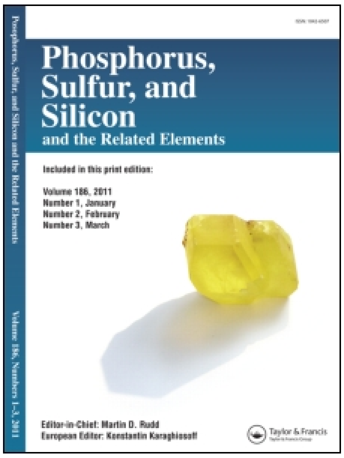

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Sax, Alexander F. and Janoschek, Rudolf(1986) 'PSEUDOPOTENTIAL CALCULATIONS ON Si_6H_6', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 1, 151 — 166
To link to this Article: DOI: 10.1080/03086648608072805
URL: http://dx.doi.org/10.1080/03086648608072805

Phosphorus and Sulfur, 1986, Vol. 28, pp. 151–166
0308-664X/86/2802-0151/$20.00/0

PSEUDOPOTENTIAL CALCULATIONS ON Si_6H_6

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The method of local pseudopotentials is applied to the calculation of the ground state structures of some isomers of Si_6H_6. The cyclic hexasilabenzene (D_{6h} symmetry) is found to be the energetically lowest structure. The question of resonance stabilization is discussed.

INTRODUCTION

The Si_6H_6 system is of considerable interest for both experimental and theoretical chemists. For experimentalists it is challenging to synthesize another "non-existent" molecule after the spectacular syntheses of disilene[1,2] and cyclotrisilane,[2] two molecules which have been sought after for many years and thought as being highly unstable. The opposite proved to be true. These syntheses have an important impact on the textbook knowledge that silicon is unable to form stable double bonds and three-membered rings. Besides these new findings the well known preference of silicon to adopt divalent instead of multiply bonded structures enlarges the number of possible claimants for the ground state structure of Si_6H_6 compared with the C_6H_6 system. Thus, non-cyclic structures and ring systems of fused small rings cannot be excluded *a priori*. From all possible structures of Si_6H_6 mainly the six-membered ring and the silicon analogue of prismane are fascinating to chemists.

The silicon analogue of benzene, hexasilabenzene (HSB), is the most prominent one. Since benzene is the prototype of aromatic molecules, questions for symmetry (D_{6h} symmetry or not), geometry, electronic structure and delocalization stabilization (i.e. resonance stabilization in older terminology) are of actual interest. Another prominent isomer of Si_6H_6 is hexasilaprismane (HSP). Its carbon analogue, being a fused 3- and 4-membered ring system, is highly strained and lies energetically about 90 kcal/mol above benzene.[3] It is questionable if such a high energetic difference is also found between HSB and HSP.

Within the scope of our investigations on silicon hydrides we have undertaken studies on the Si_6H_6 potential energy surface restricting ourselves to cyclic structures, though, as mentioned above, noncyclic structures cannot be excluded from the list of low-lying isomers. The most extensive calculations have been done on hexasilabenzene and hexasilaprismane and gave the result that both molecules are local minima on the potential energy surface and, most surprisingly, are nearly isoenergetic at the SCF level, hexasilaprismane lying 2.5 kcal/mol above hexasilabenzene.[4] Inclusion of correlation corrections yielded only a minor change in the

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energy difference. This paper is mainly devoted to a discussion of the aromatic character of hexasilabenzene, in particular to the delocalization energy.

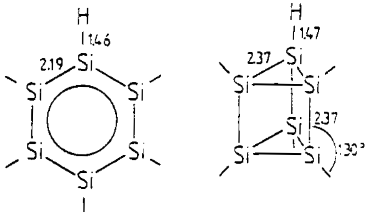
COMPUTATIONAL METHOD

For calculations of molecules with several second-row atoms it is favourable to avoid the explicit consideration of the chemically less important core electrons. This can be done by pseudopotential methods where the repulsive effect of the core on the valence electrons is simulated by a potential.[5] The pseudopotential for silicon, developed by our group has been described in detail in recent papers[6a, 6b] to which is also referred for a detailed description of the basis sets used. This pseudopotential has been applied to several silicon hydrides and proved to reproduce successfully experimental data and results of all electron calculations.[6] For the calculations on Si_6H_6 an uncontracted (3s, 3p) basis for the silicon valence shell and the uncontracted Huzinaga (3s) basis for hydrogen was used. All calculations have been done at the RHF (restricted Hartree-Fock) closed shell level. Geometry optimizations and force calculations have been performed with analytical gradient techniques using the HONDO system of programs,[7] which has been modified in the integral and gradient part for the pseudopotential.

HEXASILABENZENE

In the following we summarize the most important results of Reference 4. Hexasilabenzene (HSB) has D_{6h} symmetry with the geometry parameters given in Figure 1. The value of 2.191 Å for the SiSi bond lengths lies in between those for disilane (2.338 Å)[6b] and disilene (2.116 Å)[6b] and the SiH bond length of 1.464 Å is nearly the same as in disilene (1.461 Å).[6b]

The MO diagram of HSB has the expected benzoide pattern (Figure 2) but shows remarkable differences to that of benzene. Firstly, all orbital energies are shifted to higher energies which implies a lower ionization potential for HSB (7.2 eV vs. 9.3 eV).[8] Secondly, we note that all orbital energies lie in a smaller energy interval than the corresponding valence orbitals of benzene. Especially, the pi levels are separated only by 2.4 eV rather than by 4.3 eV as in benzene and, moreover, lie both above the highest sigma orbital, whereas in benzene the a_{2u} pi orbital lies 0.3 eV below the e_{2g} sigma orbitals. From the geometry parameters and the MO scheme one would, therefore, assume that HSB is a molecule with aromatic character but with a lower delocalization stabilization than in benzene. In order to get an impression of the electronic situation of hexasilabenzene we have plotted the total valence electron density (VED) for 5 parallel cutting planes positioned in vertical distances of 0.5 Å above the molecular plane which is cutting plane 1 (Figure 3 a–e). The plots show that the VED is concentrated in the bond regions and decreases to zero in the middle of the molecule which is a consequence of the dimension of the molecule with a diameter of the silicon skeleton of 4.38 Å. This fact points already to the main problem of a synthesis of HSB, namely the protection of the regions above and below the silicon ring against reactive molecules.



I II

FIGURE 1 Structures of hexasilabenzene (I) and hexasilaprismane (II). Interatomic distances are given in Å.

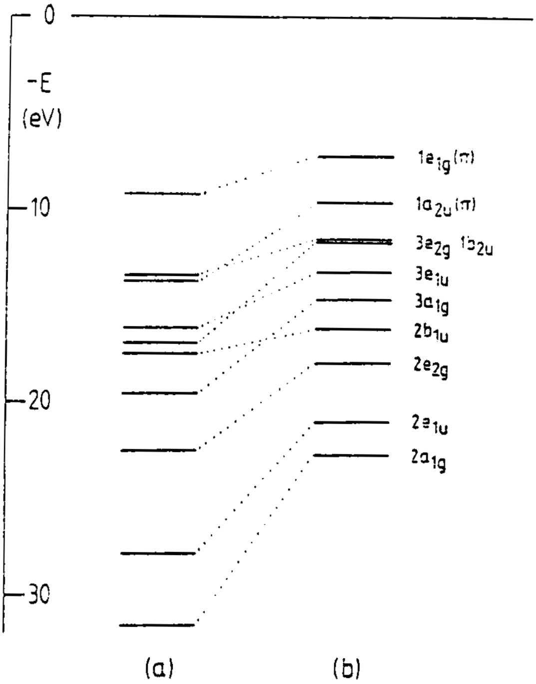
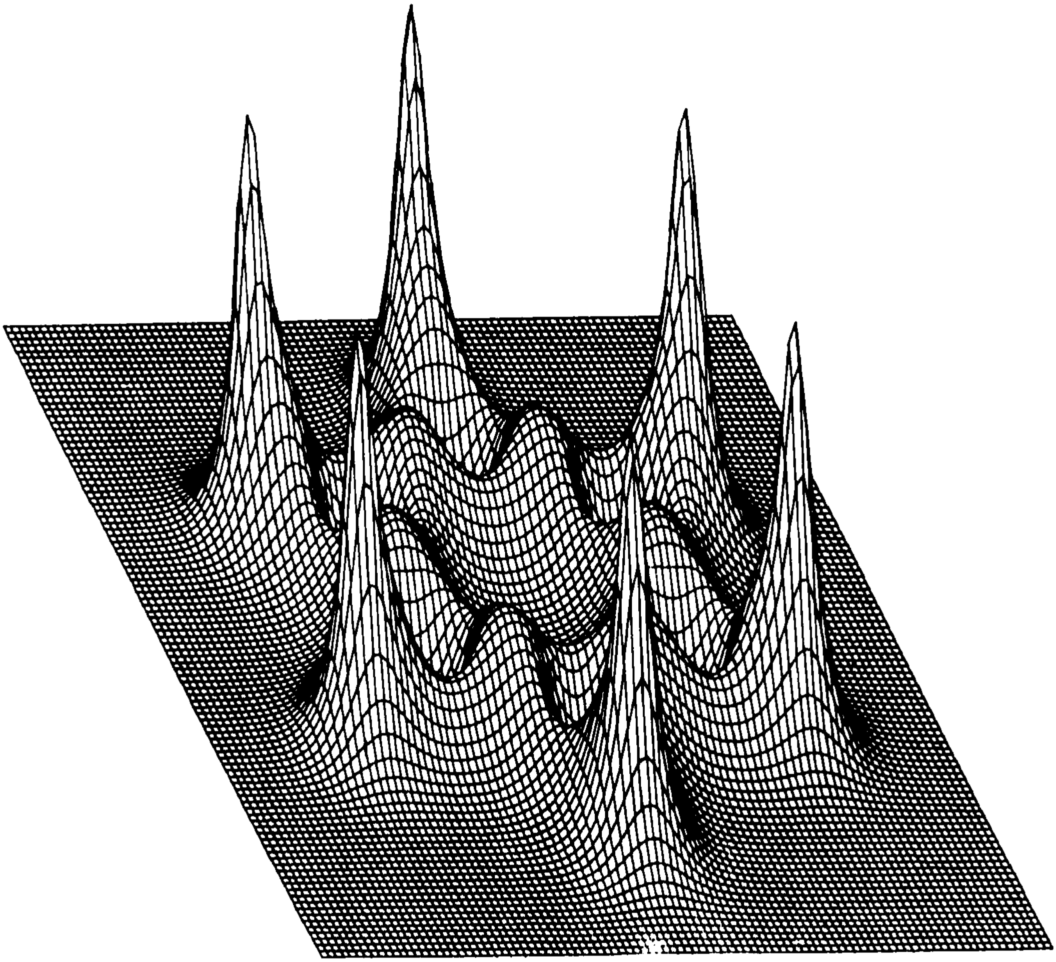


FIGURE 2 Valence MO levels of benzene (a) (from Reference 8) and hexasilabenzene (b).

The calculated vibrational frequencies show another surprising feature of HSB, inasmuch as it is a molecule with an easily distortable silicon skeleton (Table I). The normal modes with the lowest frequencies are associated with bending motions of the silicon ring with the respective wavenumbers 61 (ring puckering), 125 (SiSiSi out-of-plane bending), 186 (SiSiSi in-plane bending) and 326 (SiSiSi trigonal bending). These values have, however, still to be reduced by 10 percent to give reliable predictions for experimental frequencies. The frequencies of the corresponding modes of benzene are 707, 404, 606 and 1010 cm^{-1}.[9]

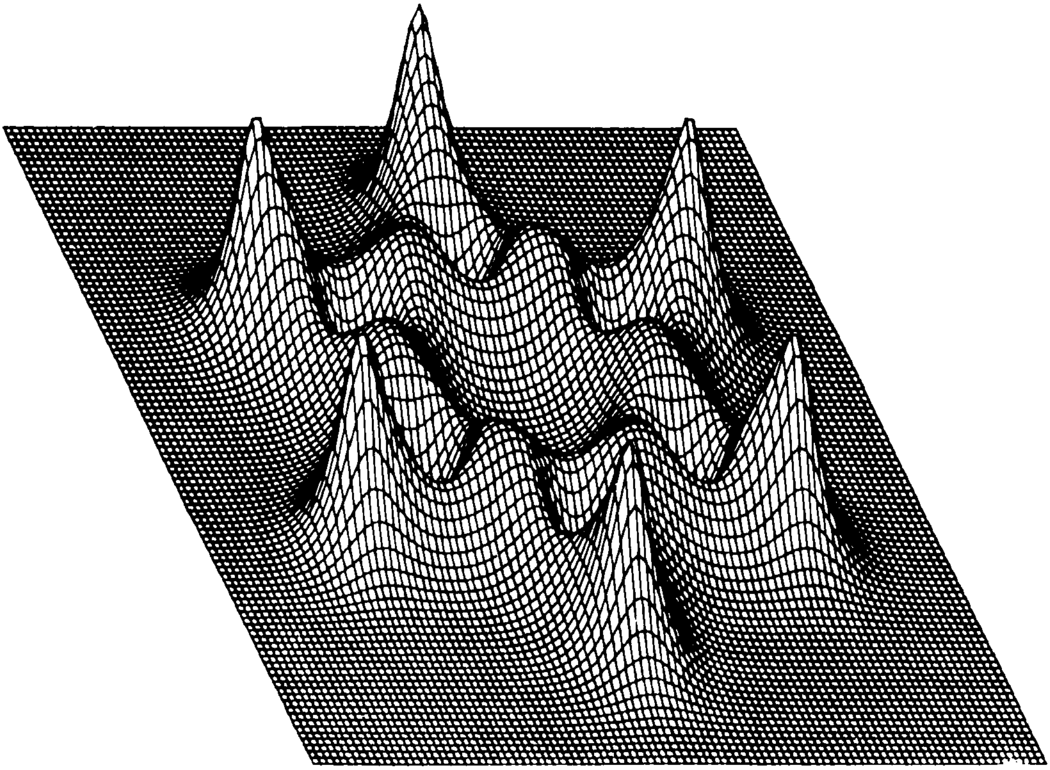
HEXASILAPRISMANE

The geometry of hexsilaprismane (HSP) is depicted in Figure 1. There is a remarkable difference to the geometry of the carbon analogue in that all silicon-silicon bond lengths are equal whereas in prismane the carbon-carbon bonds of the 3-membered rings are significantly shorter (1.500 Å) than those connecting the two rings (1.585 Å).[3] The SiSi bond length of 2.370 Å in HSP is nearly identical with that in puckered cyclotetrasilane (2.371 Å)[10] and larger than that in cyclotrisilane (2.336 Å).[11] The slightly bent bonds can be visualized by the plots of the VED in three cutting planes as indicated in Figure 4a–c. Since with our method only valence electrons are accounted for the VED is not superimposed by the density of the core

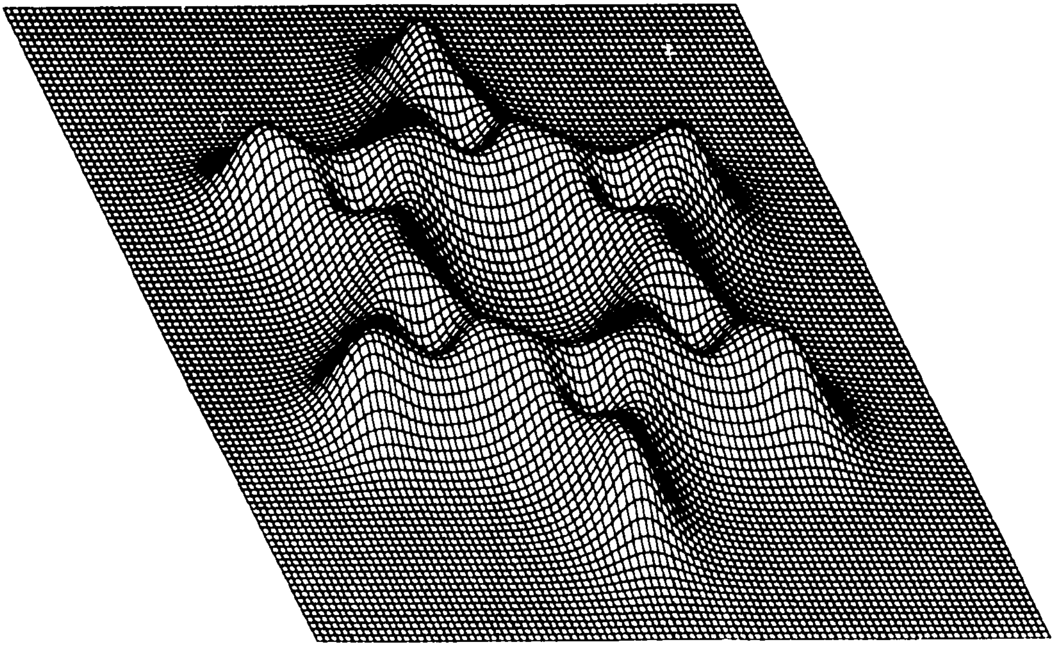


(a)

FIGURE 3 Valence electron density of hexasilabenzene, with the basal plane passing through all constituent atoms (a). The next four planes b)–e) are parallel to the basal plane with respective increments of 0.5 Å. f) is a contour plot of the valence electron density in the basal plane.

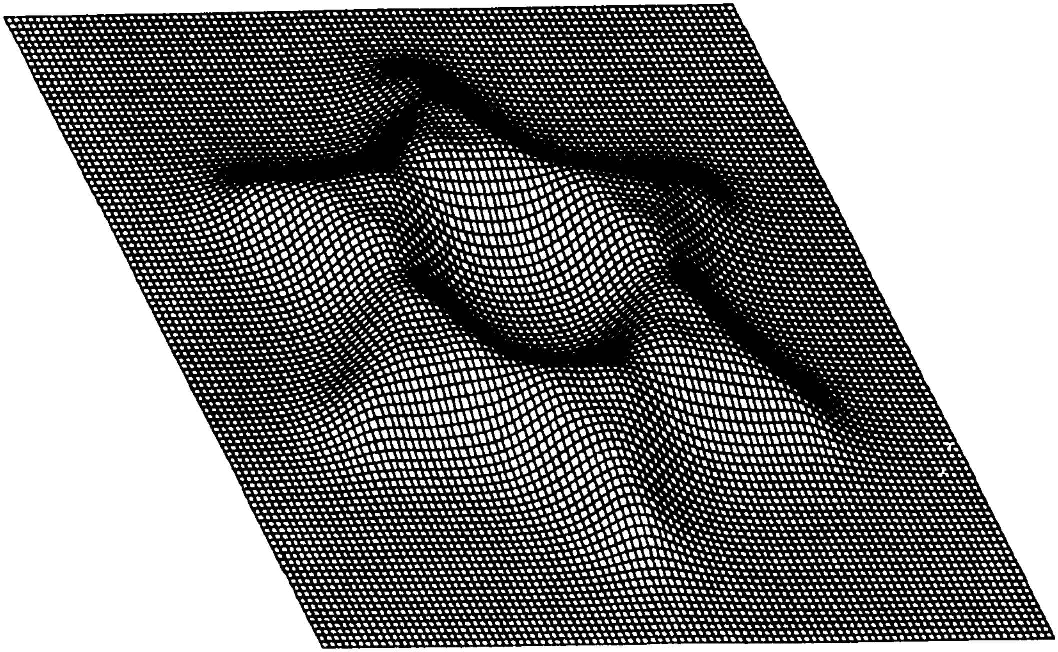


(b)

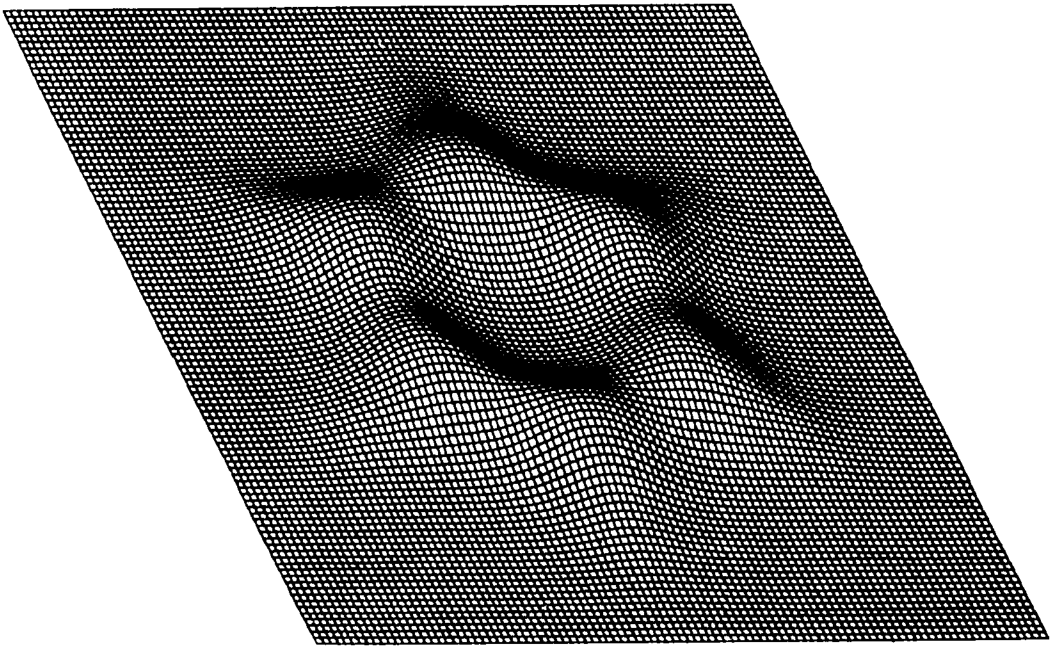


(c)

FIGURE 3 (*Continued*)

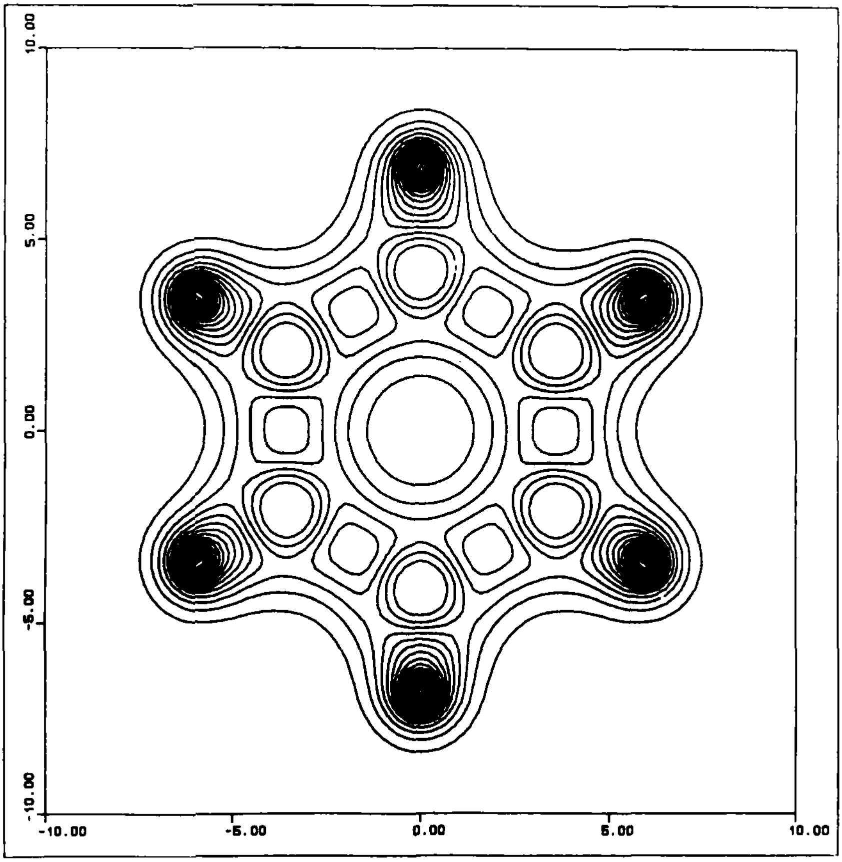


(d)



(e)

FIGURE 3 (*Continued*)



(f)

FIGURE 3 (*Continued*)

electrons and, therefore, one can easily visualize bent bonds. It has already been found for cyclotrisilane that the bonds in the small ring systems are slightly bent but considerably less than in cyclic carbon hydrides.[11] The same is true for HSP as can be seen from Figure 4. The minor distortion of the bonds in cyclic silicon hydrides is probably due to the larger distances between the centers of bond densities in silicon hydrides. This fact is also responsible for the decrease of electron density in the middle of the rings, though it does not shrink to zero in the smaller 3- and 4-membered rings as it does in HSB. From the bonding situation one can conclude that HSP has the character of a nearly unstrained silicon hydride. If one takes into account that HSP has, in contrast to HSB, a more globulary shape which can easier be protected against reactive molecules by big substituents than HSB, one would expect that HSP should be easier synthesized than HSB.

DELOCALIZATION STABILIZATION OF HEXASILABENZENE

Though aromaticity is not directly observable it is one of the central concepts in organic chemistry. It has originally developed as a means of characterizing a certain

TABLE I

Calculated harmonic vibrational frequencies of hexasilabenzene[a] and vibrational frequencies of benzene[b] (in cm^{-1})

	Si_6H_6	C_6H_6	Assignment
a_{1g}	2413 (2171)	3073	X—H stretching in-phase
e_{1u}	2406 (2165)	3064	X—H in-plane bending, in-phase
e_{2g}	2400 (2160)	3056	X—H stretching
b_{1u}	2396 (2156)	3057	X—H trigonal stretching
e_{1u}	789 (710)	1037	X—H in-plane bending
e_{2g}	784 (706)	1178	X—H in-plane bending
a_{2g}	675 (608)	1350	X—H in-plane bending in-phase
b_{2u}	665 (599)	1146	X—H in-plane trigonal bending
e_{2g}	619 (557)	1599	X—X stretching
b_{2u}	580 (522)	1309	X—X stretching (Kekule)
e_{1u}	490 (441)	1482	X—X stretching
b_{2g}	483 (435)	990	X—H out-of-plane trigonal
e_{1g}	464 (418)	846	X—H out-of-plane
e_{2u}	436 (392)	967	X—H out-of-plane breathing
a_{1g}	419 (377)	993	
a_{2u}	406 (365)	673	X—H out-of-plane in-phase
b_{1u}	326 (293)	1010	X—X—X trigonal bending
e_{2g}	186 (167)	606	X—X—X in-plane bending
e_{2u}	125 (113)	404	X—X—X out-of-plane bending
b_{2g}	61 (55)	707	X—X—X puckering

[a] To provide a more realistic comparison, the calculated frequencies have been reduced by 10 percent, following a suggestion of Y. Yamaguchi and H. F. Schaefer III, *J. Chem. Phys.*, **73**, 2310 (1980). These frequencies are given in parentheses.

[b] Experimental frequencies and assignments are from Reference 9.

type of thermally stable organic molecules that was inclined to substitution rather than addition reaction as benzene is. Most chemists will agree that this characterization of aromatic molecules still holds. A theoretical rule for the characterization of aromatic systems has been given by Hückel with his famous $4n + 2$ rule ($n = 0, 1, 2 \ldots$). The physical background of the Hückel rule was the finding that a pi electron system of $4n + 2$ pi electrons has a lower energy than a system with the same number of pi electrons in $2n + 1$ isolated double bonds. This energy lowering is caused by delocalization of the pi electrons.

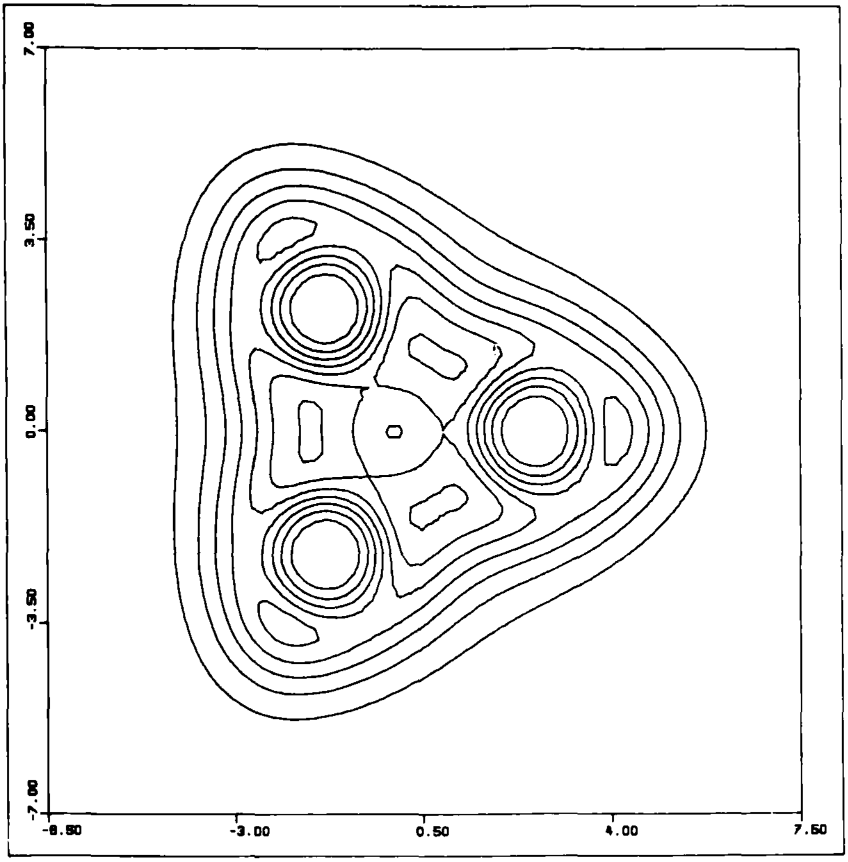
The energy difference between the aromatic molecule and the reference system with the isolated double bonds is the so called delocalization or resonance energy RE.

$$RE = E^{\pi}(\text{aromatic molecule}) - E^{\pi}(\text{reference structure})$$

High stability of aromatic molecules should be reflected by large positive resonance energies. A consequence of the delocalization of the pi electrons is, furthermore, that all bond lengths of the aromatic ring are equal. This definition abstracts totally from the chemical properties of the atoms from which the molecule is built up (e.g. electronegativity) and leads at last to a rule of thumb which is mere pi electron counting. By this abstraction process it is, however, possible to extend the concept of aromaticity to hydrocarbons with heteroatoms and, finally even to molecules containing no more carbon atoms such as borazine, hexaazabenzene, HSB and other molecules, many of which have not yet been synthesized.

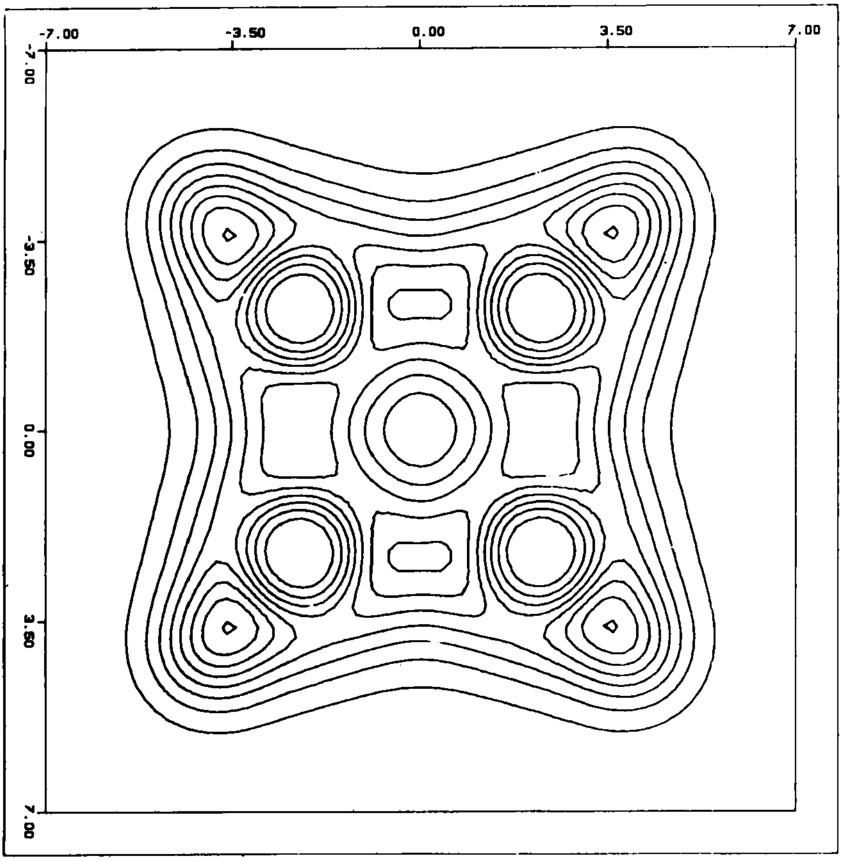
In order to compare the aromatic character of different molecules one needs a quantity that correlates well with experimental stability. It was found that RE does not even in the hydrocarbon series serve as a useful measure when molecules with e.g. different number of rings are compared. One can, however, easily derive such a quantity from RE by dividing the resonance energy by the number of pi electrons.[12] The main problem with the calculation of delocalization energies is, however, the definition of the reference structure.

In an epochal series of papers Dewar and co-workers gave a re-definition of the resonance[13] energy by a new-definition of the reference structure relative to which the resonance stabilization is calculated. The point of their work is the abandonment of cyclohexatriene with isolated double bonds as reference structure, a species chemists never work with. Instead they proposed classical polyenes as reference molecules. Since pi electrons in classical polyenes are partially delocalized C—C single bonds have considerable double bond character and, therefore, contribute to



(a)

FIGURE 4 Valence electron density of hexasilaprismane in a) a plane passing through the silicon atoms of a three-membered ring, b) a plane passing through the silicon atoms of a four-membered ring, and c) a plane passing through two hydrogen atoms and two silicon atoms and bisecting the three-membered rings.



(b)

FIGURE 4 (*Continued*)

the pi bond energy. Thus the pi energy of a polyene with n single bonds and $n + 1$ double bonds is

$$E^{\pi} \sim n E^{\pi}_{C-C} + (n + 1)E^{\pi}_{C=C}$$

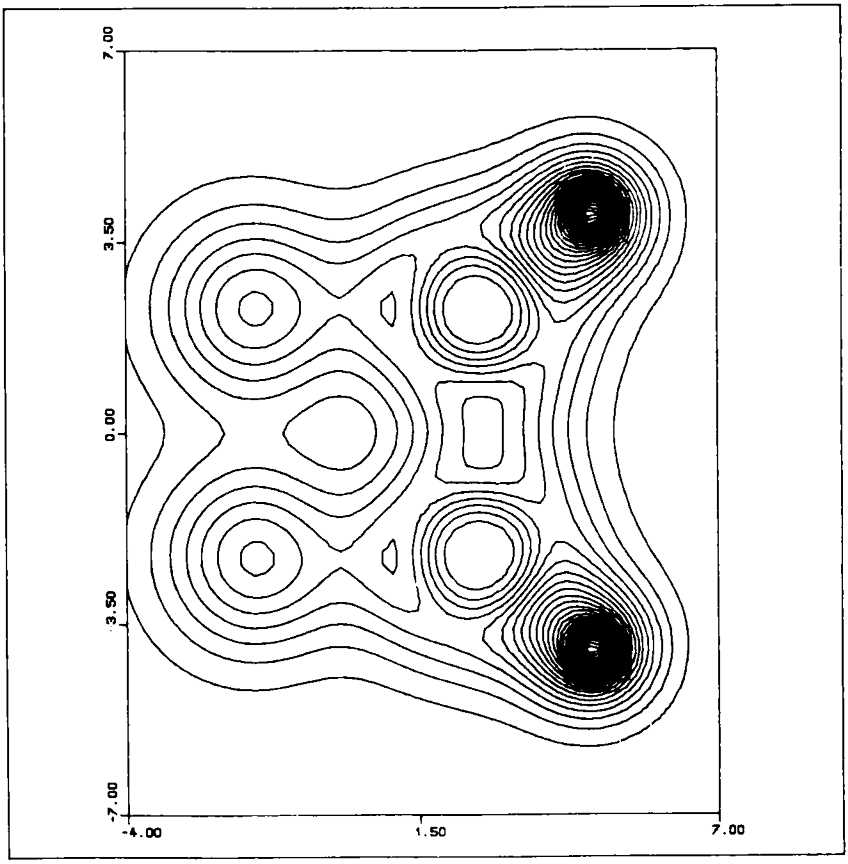
This energy expression is linear in n

$$E^{\pi} \sim n(E^{\pi}_{C-C} + E^{\pi}_{C=C}) + E^{\pi}_{C=C}$$

and allows therefore the calculation of the pi energy of any polyene. To calculate the resonance energy of an aromatic molecule with n single and double bonds one has to subtract the pi energy of the aromatic molecule from the pi energy of the reference polyene

$$RE = n(E^{\pi}_{C-C} + E^{\pi}_{C=C}) - E^{\pi}(\text{aromatic molecule})$$

This resonance energy is called Dewar type resonance energy (DRE). Because the single bonds contribute to the pi energy the values of Dewar resonance energies are smaller than the conventionally calculated values.



(c)

FIGURE 4 (*Continued*)

In the following, we discuss three theoretical quantities that can serve as index of the aromatic character of HSB. They are equivalent to Dewar type resonance energies.

1) The method of model wave functions

The method of model wave functions to calculate Dewar type resonance energies[14] is as follows:

a) One calculates the conventional resonance energy RE as difference between the reference structure with isolated single and double bonds and the aromatic molecule.

b) This energy difference must be corrected for the double bond contribution of the single bonds which is simply the conventional resonance energy of butadiene RE(butadiene).

c) Subtracting *n* times RE(butadiene) from RE gives DRE.

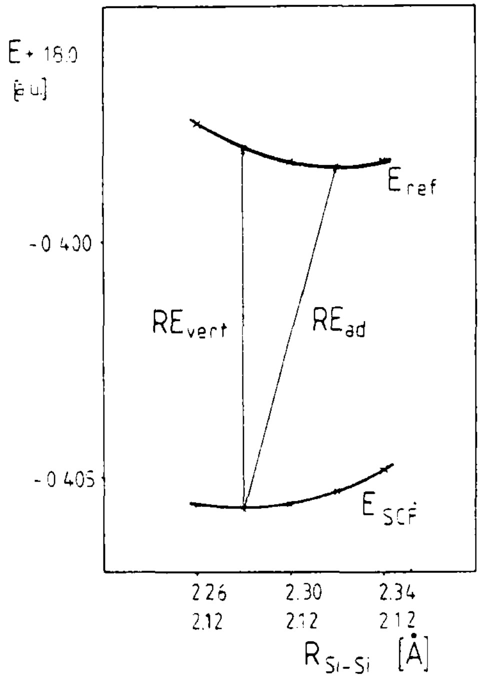


FIGURE 5 SCF energy and the energy of the reference structure of TSB as a function of the Si—Si single bond length (Si=Si 2.120 Å).

The energies of the reference structures are calculated as expectation values of model wave functions with isolated pi MOs. When resonance energies are calculated at the equilibrium geometry of the delocalized system one gets the so called vertical resonance energy, which has to be corrected for compression contributions of the sigma bonds, since the sigma bonds in the conjugated system are shortened. This correction can be done by optimizing the geometry of the reference structure with respect to the expectation value of the model wave function, giving the adiabatic resonance energy. Only these adiabatic resonance energies are used in our calculations.

Figure 5 shows the potential curves of tetrasilabutadiene (TSB) and its reference structure. Table II contains the energy values calculated for both systems. The

TABLE II

Geometry parameters and resonance energy of tetrasilabutadiene (in kcal/mol)

vertical resonance energy[a, b]	4.8
adiabatic resonance energy[b]	4.5
optimum Si—Si single bond length without resonance[a, b]	2.320 Å
optimum Si—Si single bond length (SCF)	2.280 Å

[a] Fixed geometry parameters: Si=Si: 2.120 Å, Si—H: 1.464 Å, ∢SiSiSi: 120, ∢SiSiH: 120.

[b] *Model wave function with disilene pi MOs.*

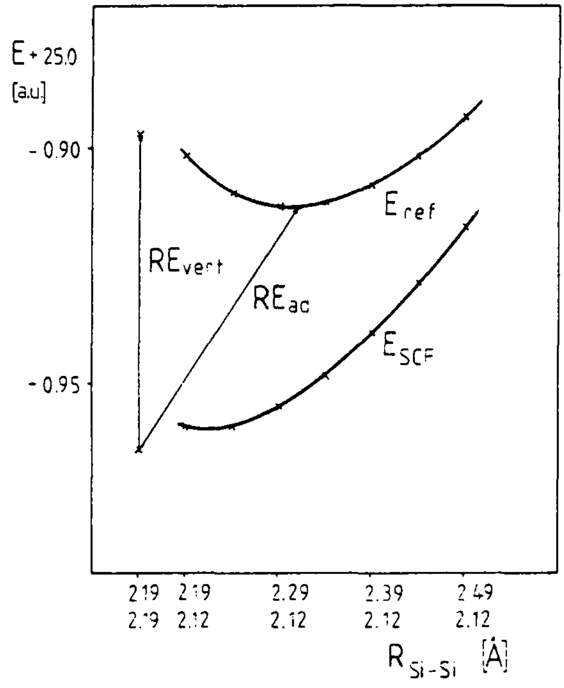


FIGURE 6 SCF energy and the energy of the reference structure of HSB as a function of the Si—Si single bond length (Si=Si 2.120 Å)

adiabatic resonance energy of TSB, i.e. the contribution to the effective single bond to the pi energy, is found to be 4.5 kcal/mol. Figure 6 and Table III show the respective results for hexasilabenzene for which the adiabatic resonance energy is calculated to be 32.7 kcal/mol. For DRE a value of 19.2 kcal/mol is finally determined. Table IV shows a comparison of our results with Kollmar's results[14] for benzene. It is obvious that HSB has a lower resonance energy than benzene.

2) Homodesmotic reactions

Since all experimental determinations of resonance energies are based on reaction enthalpies a special kind of reaction was designed to determine stabilizing effects in

TABLE III

Geometry parameters and resonance energy of hexasilabenzene (in kcal/mol)

vertical resonance energy[a,b]	42.0
adiabatic resonance energy[b]	32.7
normalized resonance energy	19.2
optimum Si—Si single bond length without resonance[a,b]	2.309 Å

[a] Fixed geometry parameters: Si=Si: 2.120 Å, Si—H: 1.464 Å, ∢SiSiSi: 120, ∢SiSiH: 120.

[b] Model wave function with disilene pi MOs.

TABLE IV

Resonance energies of butadiene, TSB, benzene and HSB (in kcal/ mol)

	butadene[a]	TSB	benzene[a]	HSB
vertical resonance energy	9.5	4.8	96.4	42.0
adiabatic resonance energy	9.3	4.5	56.0	32.7
normalized resonance energy[b]	—	—	28.2	19.2
normalized resonance energy[c]	8.3	—	24.7	19.2

[a] Resonance energies of butadiene and benzene are from Ref. 14.
[b] SCF values.
[c] Energy value with correlation corrections.

conjugated rings. An homodesmotic reaction is defined as one in which 1) there are equal numbers of heavy atoms X (X = C, N, O, Si, ...) in their various states of hybridization in reactants and products and 2) there are equal numbers of heavy atoms X with zero, one, two... H atoms attached in reactants and products. These conditions imply that there are equal numbers of each type of X—X bond (sp^3-sp^3, sp^2-sp^3, etc.) and that the various types of X—H bonds are matched as closely as possible.[15]

The homodesmotic reaction for the determination of the resonance energy of benzene and its homonuclear analogues is the following model reaction:

$$3XH_2{=}XH{-}XH{=}XH_2 \rightarrow X_6H_6 + 3XH_2{=}XH_2 \qquad X{=}C, Si, Ge, \ldots$$

With the energy values given in Table V we get a reaction energy of 20.7 kcal/mol in good agreement with the resonance energy obtained by Kollmar's method. To get an estimate of the reaction enthalpy inclusion of zero point energies would be needed. We have not, however, calculated harmonic frequencies of tetrasilabutadiene. The agreement of both estimates of the resonance energy is in any event striking.

3) Isodesmic reaction

Isodesmic reactions are defined as reactions in which there is a retention of the number of bonds of a given formal type (single, double, triple), but a change in the structural relationships between them.[16] The following method has been used by Dewar[17] to estimate the resonance energy of hexasilabenzene. We first consider the reaction

$$2\,Si_2H_4 \rightarrow TSB + 2\,H_2$$

Though we found the *trans* isomer of TSB to be lower in energy by 1.2 kcal/mol than the *cis* isomer[18] we take the energy of the cis isomer for the calculation of the

TABLE V

Total valence energies in (a.u.)

hexasilabenzene	−25.9644091
tetrasilabutadiene	−18.4072624
disilene	−9.7633933
H_2	−1.1218594

reaction energy, since the latter has already the same position of the double bonds as in HSB. The reaction energy is found to be exothermic by 1.5 kcal/mol. Next we consider the reaction

$$\textit{cis}\text{-TSB} + Si_2H_4 \rightarrow Si_6H_6 + 2\,H_2$$

If the double bonds were localized the reaction energy should be twice the value of the first reaction. We find, however, a reaction energy of −23.5 kcal/mol and, therefore, we have an extra stabilization of (23.5 − 3.0) = 20.5 kcal/mol. This stabilization energy is again in good agreement with the values of the first two methods. Dewar found with MINDO/3 a resonance stabilization energy of 8.9 kcal/mol but this value is too low due to an underestimation of resonance energies by MINDO/3. This deficiency can be seen by analogous calculation for benzene for which one gets a resonance energy of 9.2 kcal/mol.

IS HEXASILABENZENE AN AROMATIC MOLECULE?

As mentioned above DRE values are lower than the conventional RE values obtained by the older methods. For benzene, the value dropped from ~ 40 kcal/mol to ~ 24 kcal/mol. This low DRE was found at different levels of theory (Hückel, PPP, all electron SCF) with different methods. Table VI shows some of these results.

We get for HSB with the above discussed three methods DRE values of ~ 20 kcal/mol which are presented in Table VII. Kollmar found for benzene a reduction of DRE by less than 10 percent when correlation corrections were included. Assuming that the same is true for HSB, we arrive at a DRE value of 18 kcal/mol.

TABLE VI

Dewar type resonance energies of benzene (in kcal/mol)

Method	Reference	DRE
pi bond energies, PPP	13c	20.5
homodesmotic reaction, SCF, 3-21G	19	25.6
homodesmotic reaction, SCF, 6-21G*	19	23.4
model wave function, SCF, DZ	14	28.2
model wave function, SCF, DZ + corr.	14	24.7
homodesmotic reaction, experimental reaction enthalpies	15	21.2

TABLE VII

Dewar type resonance energies of HSB (in kcal/mol)

Method	Reference	DRE
model wave function	this work	19.2
homodesmotic reaction	this work	20.7
isodesmic reaction	this work	20.5
isodesmic reaction	17	9.0

From this value one could be led to the conclusion that HSB is about 75 percent as aromatic as benzene. We doubt, however, that this conclusion is valid when used in the same sense as by organic chemists.

The concept of aromaticity was introduced mainly to explain the specific reactivity of benzene and its derivatives. The delocalization stabilization alone cannot describe the aromatic character but needs properties of the transition structure of the aromatic molecule and the other reagent. As is well known isoelectronic molecules show very often great similarities in so called physical properties (e.g. geometry, electronic structure, boiling point, etc.) but may differ strongly in their reactivities. Borazine is a well known example of a molecule that is isoelectronic with benzene and, thus, shows great similarities in its physical but great differences in its chemical properties.[20] The differences are still greater when molecules with second row atoms are considered. In the case of phosphonitrilic halides even the famous Hückel rule is found to be no more valid.[20] These well known facts gave rise to serious criticism of the use of the concept of aromaticity, as developed for organic species, when generalized for its validity also for inorganic compounds.[21]

Our results support this criticism. Though we found a relatively high delocalization energy for HSB we do not believe that this results in "chemical behaviour like benzene". Otherwise this would be in contrast to all other silicon hydrides which show another chemical behaviour than their carbon analogues. A reexamination of the concept of aromaticity, as initiated by Epiotis[22] and Shaik,[23] is, therefore, to be welcomed.

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