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AB INITIO STUDY OF THE ELECTRONIC STRUCTURE OF COMPOUNDS WITH A DOUBLE BONDED SILICON ATOM: Si_2H_4

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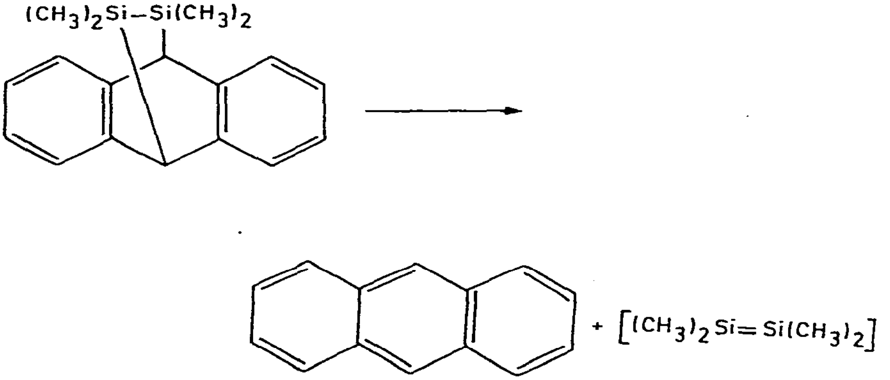
Summary

Ab initio LCAO-MO-SCF calculations have been performed on the compound disilene, Si_2H_4. The calculations indicate for the Si—Si bond length an optimized value of 2.15 Å. The electronic structure of the molecule is discussed in terms of a Mulliken population analysis, and it is shown that the 3*d* orbitals on silicon do not make a substantial contribution to the bonding.

Introduction

Several authors [1—3] have suggested the existence of $(CH_3)_2Si{=}Si(CH_3)_2$ as an intermediate in the thermal decomposition of 7,8-disila[2.2.2]octa-2,5-dienes, e.g.:



(1)

In these studies it was argued that such intermediates would involve $(p{-}p)\pi$

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bonding between the Si atoms. Some quantum mechanical calculations have been carried out for the model compound disilene, $H_2Si{=}SiH_2$. It may be assumed that replacement of the methyl groups by H atoms will have only a minor effect on the Si—Si bond type. Curtis [4] has investigated the structure of $H_2Si{=}SiH_2$ with the help of EHMO and CNDO/2 calculations, while Dewar et al. [5] have applied their MINDO/3 approach to the study of the geometry and electronic structure of this molecule.

Results and discussion

All computations were carried out with a modified version of the POLYATOM program package [6], using the same basis sets for Si and H as in an earlier study of fluorosilanes [7]. One calculation was made with inclusion of a set of Cartesian *3d* orbitals on the Si atom.

We have assumed the molecule to be in a singlet planar ground state, since calculations by both Curtis [4] and Dewar et al. [5] indicate that it is such a state at equilibrium. The ground states of the analogous molecules ethylene and silaethylene [8] also have a singlet multiplicity and a planar structure. Furthermore, the singlet state of Si_2H_4 is of interest since Peddle et al. [2] argue on mechanistic grounds that in reaction 1 $(CH_3)_2Si{=}Si(CH_3)_2$ would be produced in a singlet state.

The Si—H bond length and the H—Si—H bond angle were taken from the ab initio computations of Schlegel et al. [9] on $CH_2{=}SiH_2$. These authors carried out a complete geometry optimization for $CH_2{=}SiH_2$, resulting in a Si—H bond length of 1.479 Å and a H—Si—H bond angle of 114.2°. It is expected that these geometrical parameters will be close to the optimal parameters in $H_2Si{=}SiH_2$ for several reasons. First of all, Dewar et al. [5] find a practically constant value of 1.47 Å for R(Si—H) in $CH_2{=}SiH_2$ and $SiH_2{=}SiH_2$. Furthermore, R(Si—H) values mentioned show a striking similarity to R(Si—H) in silane, which is 1.48 Å [10], while Damrauer [11] in a CNDO/2 study of $CH_2{=}SiH_2$ calculates a value of 1.60 Å for R(Si—H). Remembering that the CNDO/2 method has a tendency to overestimate bond lengths in molecules containing second row atoms [12], and that the CNDO/2 optimized value for the Si—H bond length in silane is 1.61 Å [13], we are again led to the conclusion that the Si—H bond length is not likely to be much affected by the molecular binding state of the Si atom. The only different value for R(Si—H) stems from an ab initio study of $CH_2{=}SiH_2$ by Strausz et al. [14] who calculate this bond length to be 1.42 Å. However, a very recent and extensive ab initio study by Ahlrichs et al. [8] leads to an optimized Si—H bond distance of 1.48 Å, in $CH_2{=}SiH_2$, again pointing to constancy of the Si—H bond length.

As to the H—Si—H bond angle, most calculations predict an angle of about 115° around an sp^2 hybridized Si atom, e.g., for $CH_2{=}SiH_2$, values of 115.8° [5], 114.7° [14] and 115° [8] are reported. For $SiH_2{=}SiH_2$, Dewar et al. [5] calculated a H—Si—H angle of 111° using the MINDO/3 method.

The last geometrical parameter needed to specify completely the geometry of $SiH_2{=}SiH_2$ is the Si—Si bond distance. Assuming the values mentioned for the Si—H bond distance and the H—Si—H bond angle, we have optimized the Si—Si distance and obtained a value of 2.15 Å. This differs from the values derived by Curtis [4] using the CNDO/2 method (2.20 Å) and by Dewar et al. (2.032 Å). It is notable that our calculated bond length is close to that predicted by as simple a scheme as the Schomaker—Stevenson relation for an A—B double bond [15]:

$$R_{AB} = R_A + R_B - \beta|\chi_A - \chi_B|$$

with $\beta = 0.06$ as specified by Gordy [16]. We have obtained $R_{Si=}$ from

$$R_{C=Si} = R_{C=} + R_{Si=} - \beta|\chi_C - \chi_{Si}|$$

where $R_{C=Si} = 1.693$ Å [9], $R_C = \frac{1}{2}R_{C=C}$ in ethylene = 0.6685 Å [17] and $|\chi_C - \chi_{Si}| = 0.7$ [18]. From these values, $R_{Si=}$ is found to be 1.067 Å, corresponding to a Si—Si bond length of 2.134 Å for SiH_2SiH_2. The optimized Si—Si double bond length of 2.15 Å is also remarkably close to twice the covalent radius of double bonded silicon as given by Pauling [18].

The total energy calculated for the optimized Si—Si distance is −579.850 hartree. Inclusion of a set of 3*d* type Cartesian Gauss orbitals on each Si atom lowers the total energy by 0.068 hartree. The orbital energies calculated using the basis sets without and with 3*d* orbitals on Si are given in Table 1, together with the nature of the corresponding molecular orbitals (MO's). It is seen that, on the whole, the $4a_g$, and especially the highest two levels ($5a_g$ and $2b_{3u}$) are responsible for the σ and $\pi_\perp$ bonding between the two Si atoms.

From Koopman's theorem [19], the first vertical ionisation potential is situated at about 7.5 eV. Applying the "8% rule" [20], the probably more realistic value of 6.9 eV is obtained. This last value agrees fairly well with the ionisation potential estimated by Curtis [4] from EHMO and CNDO/2 calculations, i.e. 6.56 and 6.68 eV, respectively, but differs significantly from that obtained by Dewar et al. [5], namely 8.8 eV.

The bonding in disilene can be inferred from a Mulliken population analysis

TABLE 1

ORBITAL ENERGIES ϵ_i FOR Si_2H_4 (eV)

MO	ϵ_i		Assignment
	without 3*d*(Si)	with 3*d*(Si)	
$1a_g$	−1872.1	−1871.6	1*s*(Si)
$1b_u$	−1872.1	−1871.6	
$2a_g$	−167.5	−169.9	2*s*(Si)
$2b_{1u}$	−167.5	−169.9	
$3a_g$	−116.2	−115.5	2*p*(Si)
$1b_{3u}$	−116.0	−115.5	
$1b_{2g}$	−116.0	−115.5	
$1b_{2u}$	−116.1	−115.4	
$1b_{3g}$	−116.0	−115.4	
$3b_{1u}$	−116.1	−115.4	
$4a_g$	−20.93	−20.51	σ(Si—Si), weak σ(Si—H)
$4b_{1u}$	−17.93	−17.75	σ(Si—H)
$2b_{2u}$	−14.01	−13.92	σ(Si—H), weak $\pi_{\parallel}$(Si—Si)
$2b_{3g}$	−13.09	−13.24	σ(Si—H), weak $\pi_{\parallel}^{*}$(Si—Si)
$5a_g$	−12.36	−12.32	σ(Si—Si), weak σ(Si—H)
$2b_{3u}$	−7.64	−7.44	$\pi_\perp$(Si—Si)

TABLE 2

VALENCE OVERLAP POPULATIONS P BETWEEN THE TWO Si ATOMS IN Si_2H_4

Calculation	without 3*d*(Si)	with 3*d*(Si)
P_σ	0.754	0.795
$P_{\pi\parallel}$	−0.023	−0.031
$P_{\pi\perp}$	0.458	0.481
P_{total}	1.189	1.245

[21] of the electronic wave function. The valence overlap populations for the Si—Si bond are divided into their σ-, $\pi_\parallel$- and $\pi_\perp$-components in Table 2. It is seen that the overlap population for the Si—Si bond is greater for the σ bond than for the $\pi_\perp$ bond. The ratio of the overlap populations for the σ and $\pi_\perp$ bonds (ca. 1.60) is not altered by including 3*d* functions for the Si atoms. Their small influence on the Si—Si overlap population favours regarding them as polarisation functions, which do not participate in bond formation in a major way but which mainly affect the angular charge distribution around the Si atom. This follows also from the small coefficients with which these 3*d*(Si) orbitals enter into the MO's, their absolute values always being less than 0.06. The main effect of *d*-orbitals thus results in an increase of electronic charge in the

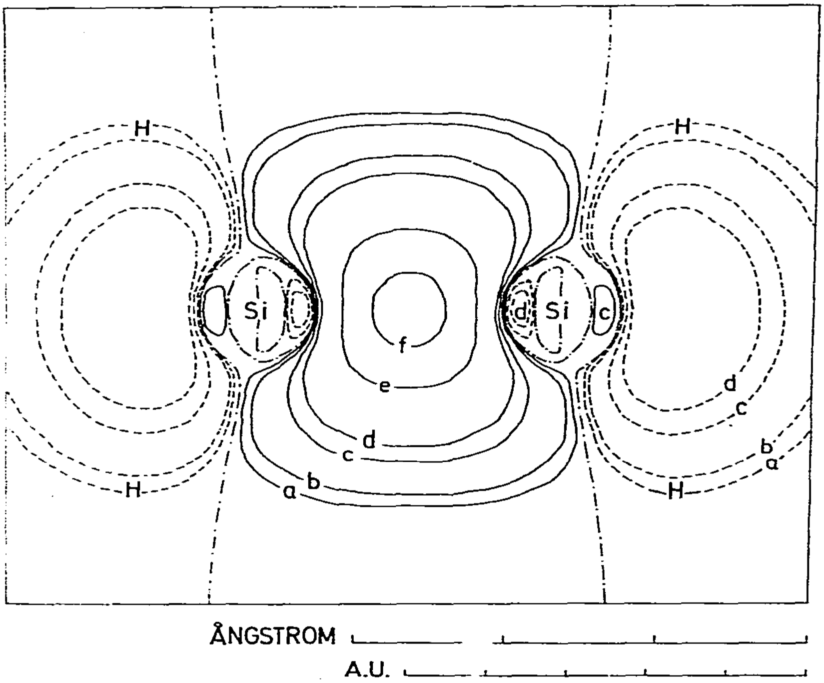

Fig. 1. Difference in electronic charge density $\Delta\rho$ (e/bohr^3) on including 3*d*(Si) functions in the basis set, for the $5a_g$ molecular orbital. The plane of the figure is the molecular plane. ——— $\Delta\rho > 0$, — — — $\Delta\rho < 0$, — · — · — $\Delta\rho = 0$. Absolute values of $\Delta\rho$: $a = 0.0001$, $b = 0.0002$, $c = 0.001$, $d = 0.002$, $e = 0.01$, $f = 0.02$.

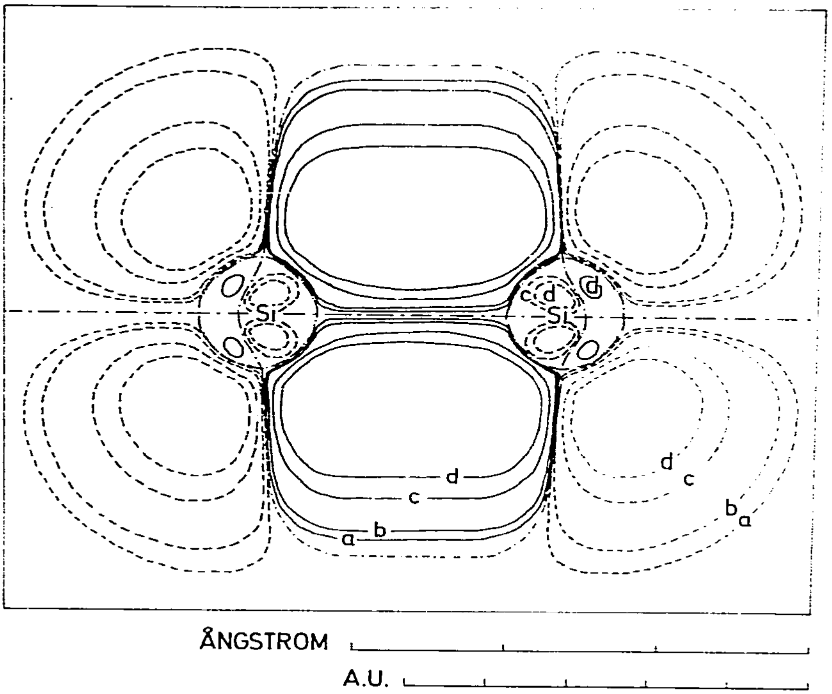

Fig. 2. Difference in electronic charge density $\Delta\rho$ (e/bohr^3) on including $3d$(Si) functions in the basis set, for the $2b_{3u}$ molecular orbital. The plane of the figure is perpendicular to the molecular plane (see also Fig. 1).

Si—Si bonding region in the $5a_g$ (σ) and $2b_{3u}(\pi_\perp)$ MO's. This may be seen from Figs. 1 and 2, which depict the change in electronic charge density of the two highest MO's upon including $3d$(Si) functions in the basis set.

The atomic charges q, calculated from the gross atomic Mulliken populations are given below:

	without $3d$(Si)	with $3d$(Si)
q(Si)	+0.168	+0.097
q(H)	−0.084	−0.049

Comparing these to the atomic charges in SiH_4, calculated with the same basis sets (0.627 and 0.486 on Si, respectively, without and with $3d$(Si)) [7] reveals the very low polarity of the bonds in this molecule.

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