Journal of Organometallic Chemistry, 66 (1974) 241—247

A THEORETICAL STUDY OF THE SILICON—CARBON DOUBLE BOND

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(Received June 27th, 1973)

Summary

CNDO/2 calculations have been carried out on $H_2Si{=}CH_2$ (I), $F_2Si{=}CH_2$ (II), $H_2Si{=}CF_2$ (III), and $F_2Si{=}CF_2$ (IV). Geometries, charge densities, bond orders, and *d*-orbital effects have been examined. The reactivity of the silicon—carbon double bond has been discussed and calculations assuming electrostatic interactions have been performed. The stability of the silicon—carbon double bond has been discussed in terms of the above mentioned calculations.

Introduction

For many years the existence of stable $(p{-}p)\pi$ bonds between carbon and the Group IV elements silicon and germanium remained in doubt. Despite a number of early reports proposing stable carbon—silicon double-bonded compounds, only the recent work of Gusel'nikov [1], Barton [2], Sommer [3], and their coworkers has placed double-bonded species on a firm experimental foundation. Such species have not been isolated, but their intermediacy has been indicated by both kinetic [1b,c] and trapping [1 - 3] experiments.

Only a few theoretical studies have appeared, and these have been recently reviewed [4,5]. Two explanations for the instability of the carbon—silicon double bond have been advanced. Firstly, second row elements have such diffuse *p*-orbitals that efficient π overlap is impossible, and secondly inner shell repulsions become important in these elements at short bond distances (i.e. those consistent with multiple bonds). Both explantions have been criticized [4] in detail and a definitive theoretical study has not appeared. Recently, extended Huckel (EHMO) and CNDO calculations, carried out by Curtis [5], have suggested that the carbon—silicon double bond is exceedingly polar and that its weakness is a result of energy mismatching of the carbon and silicon *p*-orbitals.

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We have applied the CNDO/2 (Complete Neglect of Differential Overlap) method to various fluorinated silicon—carbon double-bonded species. We have attempted to ascertain whether variations in the positions of fluorine substituents would affect the stability of the double bond. As such, we have studied silaethylene, $H_2Si=CH_2$ (I), 1,1-difluorosilaethylene, $F_2Si=CH_2$ (II), 2,2-difluorosilaethylene, $H_2Si=CF_2$ (III), and 1,1,2,2-tetrafluorosilaethylene, $F_2Si=CF_2$ (IV).

Results and discussion

The calculations reported herein were carried out using the CNDO/2 molecular orbital method developed by Pople and coworkers [7]. The parameterization of the method is unchanged from that originally proposed by Pople and Segal [8]. The CNDO method is known to predict groundstate bond lengths and angles reasonably well. The minimum energy structures were obtained by varying each geometrical parameter sequentially. Once a structure had been obtained in this manner each parameter (bond lengths and angles) in turn was changed slightly to investigate the minimum of the potential well and hopefully to avoid local small minima problems. It was found that the sequential method of parameter change led to the lowest energy structure in all cases.

Molecular geometries

The groundstate calculated geometries of the molecules I—IV are listed in Table 1. It is extremely interesting that these bond lengths and angles are transferable from molecule to molecule. For example, all FSiF or FCF angles are 110° and all HSiH or HCH angles are 120°; when carbon bears a hydrogen substituent R(Si—C) is 1.75 Å, but when the substituent is fluorine this bond stretches to 1.80 Å. Further, we have shown that the planar arrangement of atoms leads to the lowest total energy.

The bond lengths R(Si—F) and R(Si—H) are calculated to be considerably longer than we had expected. [Experimentally it is found that R(Si—H) in SiH_4 is 1.480 Å and R(Si—F) in SiF_4 is 1.54 Å]. As a result we decided to check our method by calculating the total energies of SiH_4 and SiF_4 using the longer calculated bond length (1.60 and 1.85 Å, respectively) and the "experimental" lengths [9] (1.48 and 1.54 Å). The energies calculated from the longer bond lengths are considerably higher, which indicates that the CNDO/2 method is qualitatively correct when applied to these systems, and gives confidence to the notion that the R(Si—H) and R(Si—F) bonds in the silaethylenes are, in reality, long. In addition, the silicon—carbon bond lengths are considerably shorter (1.75 or 1.80 Å) than silicon—carbon single bonds (1.89 Å).

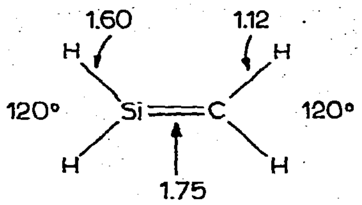
Atomic charge densities

The total charge densities of compounds I—IV listed in Table 2 indicate the enormous effect a fluorine substituent can make. A fluorine atom on silicon increases the positive character of silicon from 0.4 (with a hydrogen substituent) to 0.7, whereas the effect on carbon brings about a change from − 0.3 to 0.1. The net effect with Compounds I—IV is to vary greatly the polar

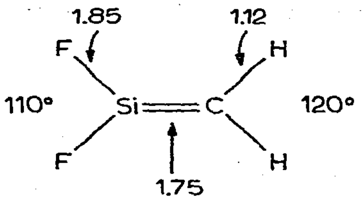
TABLE 1

CALCULATED GEOMETRIES OF PLANAR COMPOUNDS I-IV

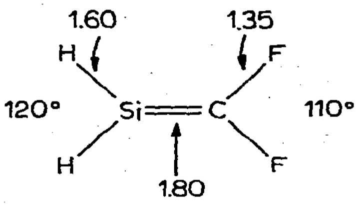
I (H_4)



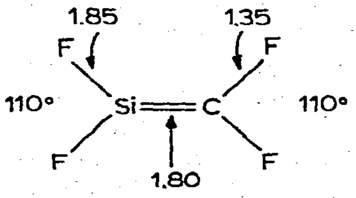
II (F_2H_2)



III (H_2F_2)



IV (F_4)



character of the Si—C bond from 0.16 in III to 1.09 in II (differences in charge densities on Si and C).

π Bond order

The π bond orders listed in Table 2 show a remarkable consistency. Compounds I—IV have considerable double bond character when the contributions of the $2p$-$3p$ and $2p$-$3p_{xz}$ types are summed. The results indicate that silaethyl-

TABLE 2

CALCULATED PROPERTIES OF COMPOUNDS I—IV

		Charge densities				π Bond Orders			Total d-orbital charge densities
		Si Atom	C Atom	Atoms on Si	Atoms on C	$2p$—$3p$	$2p$—$3d_{xz}$	Total π bond order	
I	(H_4)	0.40	−0.31	−0.12	0.07	0.74	0.63	1.37	0.76
II	(F_2H_2)	0.76	−0.33	−0.31	0.10	0.70	0.64	1.34	1.02
III	(H_2F_2)	0.31	0.17	−0.08	−0.17	0.80	0.54	1.34	0.64
IV	(F_4)	0.73	0.12	−0.28	−0.15	0.75	0.59	1.34	0.98

enes of these types have strong double bond character as measured by the π-bond order. It is worthwhile to note the large contribution of the d-orbitals to the π-bond formation.

d Orbital charge densities

As indicated in Table 2 the total d-orbital charge densities are high particularly when silicon bears fluorine substituents. We first note that whenever fluorine is attached to the silicon atom the d electron density is markedly increased. In these situations the fluorine atoms are quite negatively charged. The presumption is then that the fluorine atoms withdraw electron density from silicon through the sigma bonds allowing back donation from the lone-pair p-orbitals of the fluorine atoms. It is also interesting that the d-orbitals contain up to one electron indicating their importance in determining the electronic structure of these compounds. This taken together with the comments of the previous paragraph show that the d-orbitals are influential in double bond character determination.

π Electron densities

The π electron densities listed in Table 3 give an indication of the localization of charge densities possessing π symmetry on particular atoms. Such data are a refinement of the charge density data (Table 2) in which particular attention is drawn to electron density localized with a certain symmetry. It is interesting to note that whereas the polarity of the Si—C bond is large in compounds I, II, and IV based on total charge densities, the polarities are quite different when we consider only electron density of π symmetry. That is, compounds I and II possess highly polar Si—C bonds while III and IV do not. It would appear that fluorine has the ability to back donate electron density into the π system and that back donation is greater when fluorine is bonded to silicon than when it is bonded to carbon. This reasoning is in agreement with the discussion of the previous section. In addition we note the high and low π electron densities on silicon and carbon in III. This we believe is a result of the π inductive effect and has been discussed in detail earlier [10].

Reactivity

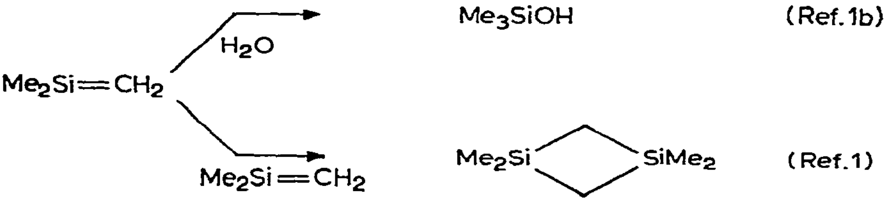
The existence of intermediates corresponding to Si—C double bonded species have been referred to amply [1 - 3]. The reactivity of such species can

TABLE 3

π ELECTRON DENSITIES OF COMPOUNDS I—IV

	Carbon	Silicon	Fluorine	Total
I	1.25	0.76		2.01
II	1.32	0.92	2 × 1.88	6.00
III	1.09	0.98	2 × 1.96	5.99
IV	1.19	1.11	on carbon 2 × 1.97 on silicon 2 × 1.88	10.00

be roughly divided into two categories: (1) reactions with polar trapping agents like H_2O, alcohols, or NH_3 and (2) self head-to-tail dimerization.



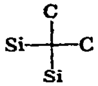
We believe we have sound evidence to suggest that there is theoretical justification for the existence of stable silicon—carbon double bonded species (to be summarized in the conclusions). This, coupled with the experimental results, encouraged us to examine the theoretical rationale for their high reactivity.

We propose that the high degree of polar character of the Si—C bond dominates the chemistry of these species (e.g. I, II, and IV) and that electrostatic interactions control the reactivity both with polar trapping agents and in the head-to-tail dimerization. To gain insight into such processes we decided to study the dimerization process. We have used the calculated charge densities of I—IV to carry out an electrostatic calculation of the approach of two Si—C double bonded species to one another. We assume that the densities do not change as the molecules approach one another and that orbital overlap between molecules is umimportant. Six different geometrical orientations have been used to calculate the potential energy curves:

(1) parallel head to head: ∥ $\begin{matrix}\text{Si—C}\\\text{Si—C}\end{matrix}$

(2) parallel head to tail: ∥ $\begin{matrix}\text{Si—C}\\\text{C—Si}\end{matrix}$

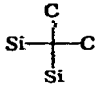
(3) parallel bisecting: ∥



(4) perpendicular head to head: ⊥ $\begin{matrix}\text{Si—C}\\\text{Si—C}\end{matrix}$

(5) perpendicular head to tail: ⊥ $\begin{matrix}\text{Si—C}\\\text{C—Si}\end{matrix}$

(6) perpendicular bisecting: ⊥



Parallel refers to those cases where the two planar double bonds approach each other with the molecular planes parallel; perpendicular refers to these planes being perpendicular to one another. Bisecting is used to indicate that the Si—C bond of one plane bisects and is perpendicular to Si—C bond of the other plane. These geometrical states are indicated in shorthand notation next to their word designation above. Table 4 summarizes the results of these 24 calculations.

Compound I has available to it only one geometrical approach which is consistent with the experimental observation that 1,3-disilacyclobutanes are dimerization products. That is, although two calculations predict strongly attractive forces, only one (the parallel head to tail dimerization) leads to a 1,3-disilacyclobutane. Such an approach is satisfying in that it represents the most simple way of looking at a head to tail dimerization.

Compound II has available to it no strongly attractive parallel mechanism, yet both the perpendicular head to tail and bisecting approaches are strongly attractive. The latter depending upon the direction of bond formation can lead to either a 1,2- or a 1,3-disilacyclobutane. It would appear that such an interesting possibility is eliminated in this case, however, because the attractive forces of the perpendicular head to tail approach become strong at a separation distance considerably greater than that for the perpendicular bisecting approach.

Compound III has only the perpendicular head to tail approach which is strongly attractive. The various approaches give quantitatively quite similar results to compound II.

Compound IV is unique among the compounds we have investigated insofar as there are *no* strongly attractive geometrical approaches for the dimerization. Of the weakly attractive interactions all are perpendicular approaches. Although the head to head and the bisecting approach become attractive at about 7 Å (distance between two Si—C bonds), the head to head approach becomes more attractive. In the perpendicular head to head approach the maximum attraction occurs at ∿ 2.9 Å, when the perpendicularly approaching fluorine atoms have approached closely the plane of the other Si—C double bond. At this maximum attraction the distance between the perpendicular fluo-

TABLE 4

ELECTROSTATIC CALCULATIONS OF THE DIMERIZATION OF COMPOUNDS I—IV

	Parallel Head to Head	Parallel Head to Tail	Parallel Bisect	Perpendicular Head to Head	Perpendicular Head to Tail	Perpendicular Bisect
I (H_4)	strongly[a] repulsive	strongly attractive	strongly repulsive	strongly attractive	strongly repulsive	strongly attractive
II (F_2H_2)	strongly repulsive	weakly attractive	strongly repulsive	strongly repulsive	strongly attractive	strongly attractive
III (H_2F_2)	strongly repulsive	attractive	strongly repulsive	strongly repulsive	strongly attractive	weakly attractive
IV (F_4)	strongly repulsive	strongly repulsive	strongly repulsive	weakly attractive	weakly attractive	weakly attractive

[a] Strong means very steep attraction or repulsion going to greater than 900 eV; weak means weak attraction or repulsion going to values between 100-500 eV.

rines and the plane is $\sim$ 1.5 Å. Bond formation between the approaching carbons under such geometrical constraints would produce a 1,2-disilacyclobutane product, which is never found experimentally under dimerization conditions.

We believe that these calculations show that predictions of reaction paths by simple electrostatic methods are consistent with experimental observations. Compounds I—III each have strongly attractive paths available to them while compound IV does not. In addition, analysis of the weakly attractive modes of approach of compound IV toward dimerization suggest that the lowest energy route will lead to a 1,2- and not a 1,3-disilacyclobutane.

Conclusions

Our calculations support the experimental data suggesting stability for the silicon—carbon double bond. Substantial π bond orders and short silicon—carbon bond lengths strongly indicate the inherent stability of such bonds. Yet we suggest that they are extremely reactive as a result of the highly polar silicon—carbon bond. Electrostatic calculations carried out on compounds I—IV, assuming that the major reactivity of such compounds results from electrostatic interactions, indicate: (1) that I can react with itself in a simple head-to-tail fashion giving a product completely analogous to that found by experiment; (2) that II and III have reaction paths open to them which give head-to-tail dimers, and (3) that IV should be either unreactive, seek some alternate reaction pathway, or give a head-to-head dimerization product. Finally, we have shown that there are large *d*-orbital contributions to compounds I—IV as well as unusual π electron density effects.

Acknowledgments

One of us (R.D.) would like to thank the National Science Foundation for partial support of this work. We also acknowledge the University of Colorado Computing Center for making computing time available to us.

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