

STEREOSPECIFICITY OF ELECTRONIC INTERACTIONS IN SILACYCLOPENTENES AND CYCLOPENTENYLSILANES*

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Charge-transfer spectra of a series of substituted silacyclopentenes and some related carbon analogues were measured in the visible region in dichloromethane solution. Tetracyanoethylene was used as an electron acceptor with the aim of proving stereoelectronic requirements of hyperconjugation. The changes of ν_{CT} with substitution at silicon are greater in cyclopentenylsilanes, in which the (HC—Si) bond is in a conformation suitable for interaction with π -system. Penning ionization spectra of analogous carbon compounds and of some silicon derivatives were also measured. Reported values of the first vertical ionization potentials correlate well with the wave-numbers of charge-transfer bands, ν_{CT} , which is evidence in support of the use of charge-transfer spectra for studying hyperconjugative interaction. Results are interpreted by means of simple orbital diagrams based on CNDO/2 wave functions. Acceptor properties of silicon can be explained by the interaction with the antibonding orbital, Σ_{π}^* , (Si—C) or (Si—X) bonds, without assuming the interaction of its *d*-orbitals. The order of acceptor strength of $\text{SiX}_3(\text{SiX}_2)$ group ($\text{X} = \text{F} > \text{Cl} > \text{H} > \text{CH}_3$) is in harmony with this explanation.

As it has already been experimentally and theoretically shown several times¹⁻³, manifestations of hyperconjugation are extraordinarily dependent on the conformation of the molecules. Bock⁴ showed on the basis of CNDO/2 calculations that the conformation of allylsilane, in which the (H_2C —Si) bond is parallel to the π -system, is c. 0.43 eV more stable than the conformation in which the (H_2C —Si) bond lies in the nodal plane of the π -system. Using correlation diagrams for these two conformations, the author illustrates mechanisms of the intermolecular interaction. However, individual conformers do not differ in their stability to the extent that conformational nonrigidity of the system could be neglected.

For that reason series of silacyclopentenes and cyclopentenylsilanes I—III ($\text{M} = \text{C}$, $\text{X} = \text{H}$; $\text{M} = \text{Si}$, $\text{X} = \text{F}$, Cl , H , CH_3) were prepared and studied. The rigid skeleton of the molecule of these compounds ensures a stable conformation, which renders it possible to discuss individual mechanisms of interaction separately on the basis of the perturbation theory and of the symmetry of the molecule.

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EXPERIMENTAL

Trimethylsilylcyclopentene-3 was prepared by reaction of chlorocyclopentene⁵ with trimethylchlorosilane in tetrahydrofuran⁶. B.p. 142°C, n_D^{20} 1.4472 (ref.⁷ b.p. 144°C, n_D^{20} 1.4560; ref.⁸ b.p. 99–100°C, n_D^{20} 1.4488; ref.⁶ b.p. 135–140°C). For C₈H₁₆Si (140.09) calculated: 68.48% C, 11.49% H; found: 68.35% C, 11.40% H.

Trichlorsilylcyclopentene-3 was prepared by a modified Kumada's procedure⁸. A mixture of 40 ml of trichlorosilane, 10 ml of cyclopentadiene, 10 mg of bis(benzonitrile)palladium dichloride, and 0.1 g of triphenylphosphine was heated in a sealed glass ampoule at 100°C for 48 h. After removal of unreacted compounds by distillation under reduced pressure, the expected derivative was obtained as a sole product in a 60% yield. The use of tributylphosphine in place of triphenylphosphine gave only a 15% yield. B.p. 75°C/20 Torr (ref.⁷ 43–45°C/5 Torr). For C₅H₇SiCl₃ (201.44) calculated: 52.79% Cl; found: 52.28% Cl.

TABLE I

Physical Constants of Studied Compounds and Wavenumbers ($10^3 \cdot \text{cm}^{-1}$) of Their Charge-Transfer Bands with Tetracyanoethylene in Dichloromethane

No	Compound	B.p., °C/Torr		n_D^{20}		ν_{CT}
		found	lit.	found	lit.	
1	Trimethylsilylcyclopentene-3 ^a	142	145 ⁷	1.4472	1.4488 ⁸	20.1
2	Trichlorsilylcyclopentene-3	75/20	43–45/5 ⁷	—	1.4480 ⁷	28.1
3	Silylcyclopentene-3	82	—	1.4595	—	23.8
4	1,1-Dichloro-1-silacyclopentene-3	134–136	134–136 ¹²	1.4780	1.4780 ¹²	27.5
5	1-Silacyclopentene-3	69–70	69–70 ¹²	1.4658	1.4658 ¹²	25.6
6	1,1-Dimethyl-1-silacyclopentene-3	101–102	101–102 ¹²	1.4448	1.4448 ¹²	24.1
7	1,1-Difluoro-1-silacyclopentene-3	66–67	66–67 ¹²	1.3852 ¹²	1.3852 ¹²	29.1
8	1,1-Dichloro-3-methyl-1-silacyclopentene	157–158	157–158 ¹²	1.4784	1.4784 ¹²	23.7
9	1,1,3-Trimethyl-1-silacyclopentene-3	116–117	116–117 ¹²	1.4504	1.4503 ¹²	21.6
10	3-Methyl-1-silacyclopentene-3	85	85 ¹²	1.4618	1.4618 ¹²	22.4
11	1,1-Difluoro-3-methyl-1-silacyclopentene-3	81–82	81–82 ¹²	1.3942	1.3942 ¹²	25.3
12	2-Methyl-2-butene	37	38 ¹⁰	1.3862	1.3859 ¹⁰	21.6
13	Cyclopentene	42	42 ¹⁰	1.4222	1.4223 ¹⁰	24.7
14	1-Methylcyclopentene-1	75	75 ⁹	1.4295	1.4326 ⁹	20.7
15	1-Methylcyclopentene-3	66–68	64.9 ¹¹	1.4221	1.4207 ¹¹	24.5
16	Cyclohexene	84–85	84 ¹⁰	1.4444	1.4464 ¹⁰	24.0
17	Cycloheptene	113–114	114	1.4571	—	23.8

^a See data in Experimental part.

Silylcyclopentene-3 was obtained by reduction of the trichlorosilyl derivative with lithium aluminium hydride in dibutyl ether. The product was distilled directly from the reaction mixture through a short column. Traces of dibutyl ether were removed by preparative gas chromatography. B.p. 82°C, n_D^{20} 1.4595. For $C_5H_{10}Si$ (98.09) calculated: 61.16°C, 10.19% H; found: 60.62% C, 10.21% H.

1,1-Dichloro-1-silacyclopentene-3 was obtained by pyrolysis of hexachlorodisilane in the presence of 1,3-butadiene in a flow apparatus¹².

1,1-Dichloro-3-methyl-1-silacyclopentene-3 was obtained by pyrolysis of hexachlorodisilane in the presence of isoprene¹².

Other derivatives were obtained in the usual way from appropriate chloro-substituted derivatives by their reduction with lithium aluminium hydride, methylation with methylmagnesium bromide or by fluorination with antimony trifluoride. Their physical constants are given in Table I. The carbon analogues were prepared by reported procedures; in the table are therefore recorded only their physical properties and the references to the literature. The purity of all the compounds was checked by gas chromatography; the substances all contained less than 1% of impurities.

Tetracyanoethylene (*purum*, Fluka) was used without further purification. Dichloromethane (analytical purity grade, Lachema) was washed with sodium carbonate solution, dried over calcium chloride and distilled through a 1 m column filled with ceramic rings. The fraction collected at 39–39.5°C was stored in a dark flask over Nalsit 4A molecular sieve.

Charge-transfer spectra of all the compounds mentioned with tetracyanoethylene as an acceptor were measured in dichloromethane solution with a Specord, Zeiss, spectrometer (Jena, DDR) in the 15000–35000 cm^{-1} region under the conditions reported in a previous work¹³. As estimated, the maxima of the bands were read with the accuracy of $\pm 100 cm^{-1}$. The results are summarized in Table I. In the case of cyclopentene, the addition of tetracyanoethylene caused a fast discoloration of the yellow solution of the complex, presumably due to a consecutive reaction.

Spectra of Penning ionization. Absolute ionization potentials were determined with respect to benzene as a standard (9.24 eV (ref.¹⁴)). The low energy of the exciting particle ($Ar^3P_2 =$

TABLE II

Values of First Ionization Potential of Some Compounds Studied Obtained by Penning Ionization with Metastable 3P_2 State of Argon

Compound	IP _a , eV	IP _v , eV	$\Delta\nu_{cm^{-1}}^a$	$\nu_{C=C}^b$
2-Methyl-2-butene	8.68	8.86	1 490	1 680 ²⁹
Cyclopentene	9.06	9.23	1 390	1 611 ³⁰
1-Methylcyclopentene-1	8.60	8.78	1 410	1 658 ³⁰
1-Methylcyclopentene-3	8.91	9.08	1 395	1 615 ^{31,c}
				1 658

^a Fine vibrational structure of the first band — the $\nu(C=C)$ frequency in the ground state of molecular cation; an accuracy of $\pm 40 cm^{-1}$ for all compounds; ^b Raman liquid; ^c Doublet.

= 11.54 eV) allowed to measure only the first ionization potentials. The measurements were carried out on a high resolution instrument^{15,16}. The obtained values of adiabatic and vertical ionization potentials are recorded in Table II.

RESULTS AND DISCUSSION

The correlation of the wavenumber of the band maxima of charge-transfer complexes with the values of the first ionization potentials taken from the literature¹⁷⁻¹⁹ is graphically represented in Fig. 1. With the aim of complementing the data not available in the literature, the Penning ionization spectra of some carbon analogues were measured. The Penning ionization differs from the photoelectron spectroscopy in the nature of the exciting particles. In place of photons, it makes use of metastable particles, in this case the ³P₂ metastable state of argon (Fig. 3). Owing to the possibility of fine specific interactions between a molecule and the exciting particle, the spectra differ in some cases from usual photoelectron spectra¹⁶. This circumstance made it impossible to measure the spectra and ionization potentials of all the silicon derivatives under study. Also due to the above mentioned interactions the values of ionization potentials of carbon analogues are shifted relative to the values obtained by photoelectron spectroscopy and do not lie on the regression line (Fig. 1). The regression line has the following form:

$$\nu_{CT}(10^3 \cdot \text{cm}^{-1}) = (8.200 \pm 0.570) \text{IP (eV)} - (50.19 \pm 0.53), \quad r = 0.986.$$

The values of ionization potentials obtained by Penning ionization were not included. When these values are considered, the correlation coefficient is 0.981, but the slope of the regression line is worse (8.930 ± 0.580).

It is worthy of note that the same regression equation also describes the values

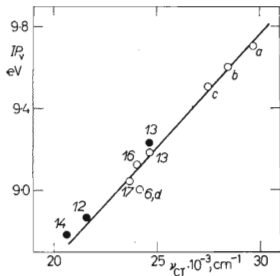
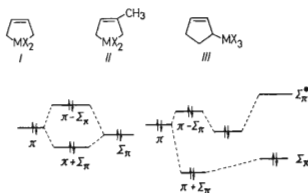


FIG. 1

Dependence of Wavenumbers of Charge-Transfer Bands of Studied Compounds with Tetracyanoethylene as Electron Acceptor on Values of First Vertical Ionization Potentials *a* 2,2-Dimethyl-3-butene, *b* 2,2-dimethyl-4-pentene, *c* allylsilane, *d* allyltrimethylsilane (ν_{CT} taken from ref.¹³). IP_v 's obtained by photoelectron spectroscopy (○) and Penning ionization (●).

of ionization potentials of the higher cycloolefins and allylsilanes. Heilbronner has also shown¹⁷ that the first ionization potential of *cis*-cycloolefins corresponds to ionization from the π orbital. This fact, along with the results obtained by Schweig¹⁸ on the basis of a study of photoelectron spectra and quantum chemical calculations by the CNDO/2 method, served in this work as the basis for the interpretation of observed charge-transfer spectra.



Contrary to cyclopentene, silacyclopentenes are planar²⁰⁻²². The highest occupied molecular orbital (HOMO) can be depicted on the basis of CNDO/2 wave functions¹⁸ as the antibonding combination of (HOMO) π orbital of *cis*-butene with the Σ_π combination of $\sigma(\text{Si}-\text{X})$ orbitals (Fig. 2). The ($\text{H}_2\text{C}-\text{Si}$) bond now lies in the plane of the ring and due to symmetry cannot interact with π -orbitals. The values of $\Delta\nu_{\text{CT}} = \nu(\text{R}-\text{SiCl}_3) - \nu(\text{R}-\text{Si}(\text{CH}_3)_3)$ are quite in harmony with this assumption. Such a possibility exists, however, in substituted allylsilanes¹³ and cyclopentenylsilanes (III), which results in higher $\Delta\nu$ values ($\Delta\nu$ (allylsilanes) = 6200 cm^{-1} ,

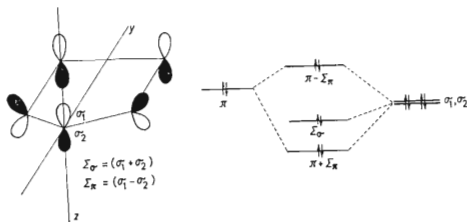


FIG. 2
Schematic Representation of the Highest Occupied Orbital (HOMO) $_{\pi}$ of Cyclopentene and the Corresponding Orbital Diagram of Its Formation

$\Delta\nu$ (III) = 8000 cm^{-1}), compared to silacyclopentenes ($\Delta\nu$ (I) = 3400 cm^{-1} , $\Delta\nu$ (II) = 2100 cm^{-1}). In compounds (I) and (II) only interaction of the HOMO orbital of *cis*-2-butene with the Σ_{π} and Σ_{π}^* , or d_{yz} orbital may take place due to symmetry. On the basis of correlation diagrams Σ_{π}^* and d_{yz} orbitals of silicon cannot be distinguished. This could be possible only on the basis of quantum chemical calculations with inclusion of configurational interaction. The arguments of the perturbation theory support, however, the participation of the Σ_{π}^* orbital¹³.

The $\pi - \Sigma_{\pi}$ combination of the highest occupied orbital corresponds to a decrease of ionization potential relative to a π -standard. The participation of Σ_{π}^* orbitals, which increases with increasing electronegativity of substituents on silicon, leads on the contrary to an increase of ionization potential, as shown in the correlation diagram.

The values of ν_{CT} for all series studied agree with this assumption. Correlation diagrams show also the effect of the π -system on the resulting values of ν_{CT} . Thus, for example, $\Delta\nu = [\nu(5) - \nu(13)] = 900 \text{ cm}^{-1}$ is smaller than $[\nu(10) - \nu(14)] = 1700 \text{ cm}^{-1}$, which is quite understandable from correlation diagrams. The introduction of the methyl group to *cis*-2-butene, giving 2-methyl-2-butene, leads to an increase in HOMO energy (compare ionization potentials of *cis*-2-butene¹⁸ 9.33 eV

and 2-methyl-butene 8.86 eV), which results in a greater interaction of the $\pi - \Sigma_{\pi}$ orbital with the Σ_{π}^* orbital, and then to a greater additional decrease in HOMO energy. This effect is even more distinct when comparing $\Delta\nu[\nu(14) - \nu(9)] = -900 \text{ cm}^{-1}$ and $\Delta\nu[\nu(13) - \nu(6)] = +600 \text{ cm}^{-1}$. From the foregoing it is obvious that the order of acceptor strength of silicon depends above all on the substitution on silicon and only to a lesser extent on the type of the attached π -system.

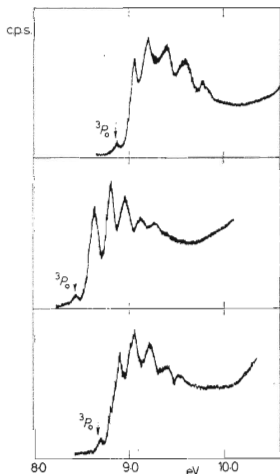


FIG. 3

Penning Ionization Spectra of Some Compounds Studied (12, 13, 14 from the bottom)

In the series of silacyclopentenes (*I*) this order is $\text{SiF}_2 > \text{SiCl}_2 > \text{SiH}_2 > \text{CH}_2 > > \text{Si}(\text{CH}_3)_2$, while in series *II* it is $\text{SiF}_2 > \text{SiCl}_2 > \text{SiH}_2 > \text{Si}(\text{CH}_3)_2 > \text{CH}_2$. This seems to indicate that in the latter series silicon affects the order only by its +I effect. A description of this type does not yield any information concerning the mechanism of transfer of substituent effects and, furthermore, it is not able to explain why the influence of the +I effect is not observed *e.g.* in series *I*. Similar problems relating to the +I effect of alkyl groups were discussed *e.g.* by Heilbronner¹⁷. This clearly demonstrates the limitation of the classical concepts of the different effects and the necessity of their substitution for corresponding orbital equivalents, such as *e.g.* Hoffmann's concept of "through space" or "through bond" interaction^{23,24}. One of the additional reasons in support of Hoffmann's interpretation is the recently studied effect of stereospecificity of σ inductive effect²⁵. The participation of *d* orbitals in the compounds $(\text{CH}_3)_4\text{X}$ ($\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn},$ and Pb) has recently been rejected in an excellent work by Lappert²⁶ only on the basis of symmetry rules. The only important interaction which is exhibited in the photoelectron spectra of these compounds is "through space" interaction.

The importance of low lying antibonding orbitals has convincingly been shown also by Schweig²⁷ who used the example of interactions in $\text{H}_3\text{Si}-\text{CH}_2-\text{CH}_2^-$. The author found that these orbitals stabilize syn-clinal conformation so that it is the most stable one, in contradistinction to the rules suggested by Hoffmann¹. However, it was Hoffmann who pointed out²⁸ the importance of the interaction with antibonding orbitals and made the suggestion to term this phenomenon "superjacent orbital interaction".

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