

HYPERCONJUGATION IN SILAACENAPHTHENES*

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Charge-transfer spectra of a series of substituted silaacenaphthenes with tetracyanoethylene were measured in dichloromethane solution. Wavenumbers of ν_{CT} increase in the sequence $\text{Si}(\text{CH}_3)_2 < < \text{SiH}_2 < \text{SiCl}_2 < \text{SiF}_2$. Electron-accepting properties of the silyl substituents can be explained in terms of interaction with low lying antibonding orbitals of $\sigma^*(\text{Si}-\text{X})$ bonds, without considering $(p-d)_\pi$ bonding.

This work continues our previous studies of CT spectra of substituted phenylsilanes¹ and 9,9'-silafluorenes² on the basis of which we concluded that $(p-d)_\pi$ bonding has not necessarily be invoked to explain electron-accepting properties of silyl substituents and further that the same conclusions are obtained by considering a hyperconjugation mechanism which in orbital diagrams is visualized by interaction with $\sigma^*(\text{SiX})$ orbitals (the so-called superjacent orbital interaction)³.

EXPERIMENTAL

Synthesis of substituted silaacenaphthenes was reported earlier⁴, along with characterization of the compounds. Naphthalene (*p.a.*, Lachema Brno) and tetracyanoethylene (*puriss.*, Fluka A. G.) were used without further purification. Acenaphthene (pure, Lachema, Brno) was recrystallized from ethanol. Charge-transfer spectra were recorded on a double-beam prism Specord spectrometer (Zeiss, Jena, GDR) in 13000–30000 cm^{-1} region in dichloromethane solution with tetracyanoethylene as an electron acceptor. Measurement conditions were the same as in our previous work⁵. Compounds under study give two, well separated CT bands in visible region. Their wavenumbers are listed in Table I.

RESULTS AND DISCUSSION

With regard to a great similarity between CT spectra of all the derivatives studied and the CT spectrum of naphthalene it is obvious that the introduction of the CH_2-SiX_2 bridge influences only little the positions of highest occupied naphthalene π molecular

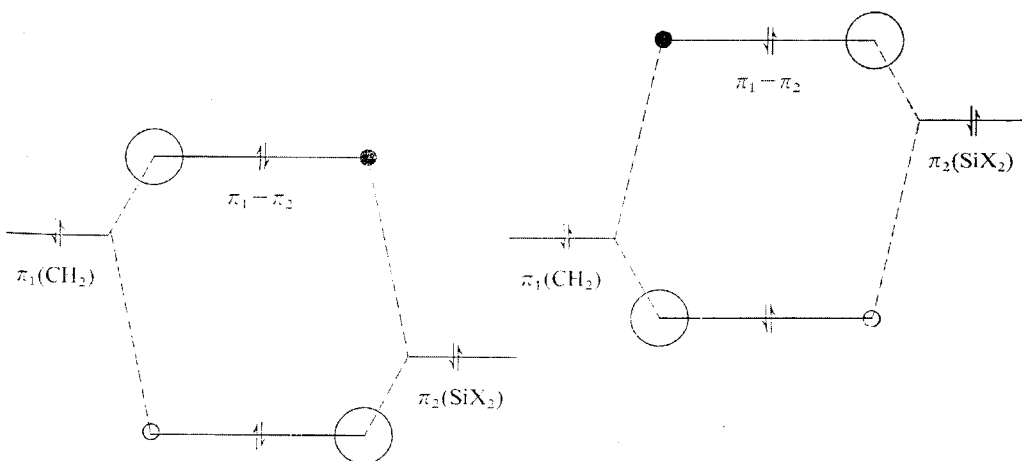
* Part CXLIII in the series¹ Organosilicon Compounds; Part CXLII: This Journal 41, 2708 (1976).

TABLE I
Wavenumbers of CT Bands (10^3 cm^{-1}) of Studied Compounds with Tetracyanoethylene as Electron Acceptor in Dichloromethane

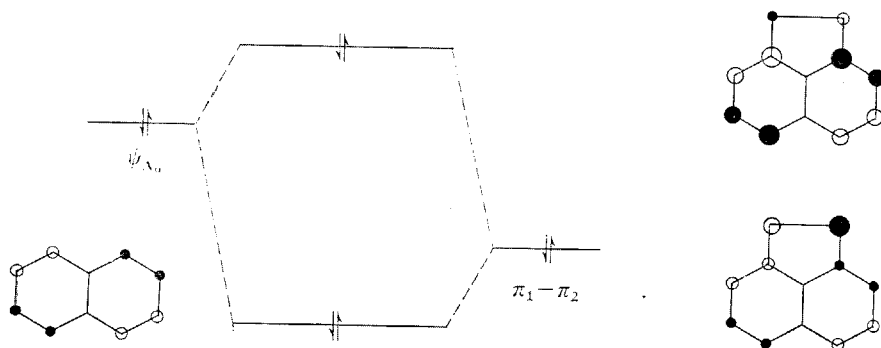
| Compound | $\nu_{\text{CT(I)}}^a$ | $\nu_{\text{CT(II)}}^a$ |
|---------------------------------|------------------------|-------------------------|
| Naphthalene | 18.1 | 23.3 |
| Acenaphthene | 15.5 | 22.7 |
| 1-Silaacenaphthene | 16.4 | 22.8 |
| 1,1-Dimethyl-1-silaacenaphthene | 16.0 | 22.3 |
| 1,1-Dichloro-1-silaacenaphthene | 18.1 | 24.0 |
| 1,1-Difluoro-1-silaacenaphthene | 18.4 | 24.1 |

^a CT band maxima were read with an estimated accuracy of $\pm 100 \text{ cm}^{-1}$.

orbitals. Therefore, the effect of this bridge can be considered as a weak perturbation and interpretation can be based on orbital diagram regarding a molecule of substituted silaacenaphthenes as composed of localised skeletons of naphthalene and $\text{CH}_2\text{—SiX}_2$. It becomes evident that only group orbitals of the $\text{CH}_2\text{—SiX}$ group with π symmetry ($\sum\pi$) may interact with naphthalene π orbitals. Their formation is depicted in Scheme 1 which shows also the effect of substituent X on the energy and shape of these orbitals. As found by HMO calculations, the highest occupied MO of naphthalene has the symmetry A_u that makes the orbital suitable to interact with a $\pi_1\text{—}\pi_2$ orbital. This interaction is shown in Scheme 2.

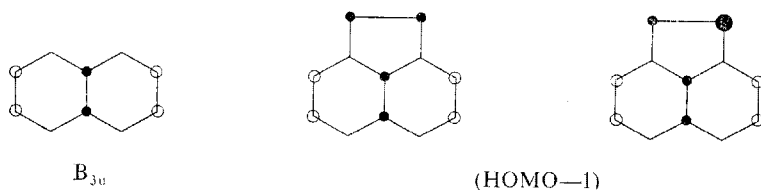


SCHEME 1



SCHEME 2

The sequence of $\nu_{CT(I)}$ values speaks for increasing electron-accepting effect of silyl substituents in the order $\text{Si}(\text{CH}_3)_2 < \text{SiH}_2 < \text{SiCl}_2 < \text{SiF}_2$, which is identical with the trend in ν_{CT} reported by us for series of substituted phenylsilanes¹, silafluorenes² and silacyclopentenes^{6,7}. These, on the basis of HMO and CNDO/2 calculations and symmetry analysis, prefer hyperconjugation mechanism of effects of silyl substituents. The same trend is observed also for the wavenumbers of the second CT band. In this case the effect of substituent X is, however, by far weaker, in agreement with HMO calculations according to which the second highest occupied molecular orbital of naphthalene is of the symmetry B_{3u} with nodal planes passing through atoms C_1C_4 and C_6C_9 (Scheme 3). The position of the second CT band would to the first approximation (neglecting interaction of $\pi_1 - \pi_2$ orbital with directly nonbonded atoms C_2 ,



SCHEME 3

C_9 and C_{10}) be essentially independent of substitution. In addition to the above-mentioned second-order effects (compare $\nu_{CT(II)}$ for naphthalene and acenaphthene) a weak dependence observed for silaacenaphthenes could be caused also by lowering in symmetry and, as a result, by nonuniform electron distribution in fragments CH_2 and SiX_2 .

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