The Ultraviolet Spectra of *p*-Bis(pentamethyldisilanyl)benzene and Related Compounds

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SINCE Hague and Prince[1] first reported the interesting u.v.-spectral properties of organopolysilanes systematic studies of the u.v. spectra of organopolysilanes have been undertaken.[2,3]

We report on the interesting u.v. spectra of *p*- and *m*-bis(pentamethyldisilanyl)benzene and related compounds, which are the first examples of u.v. spectra observed for d_π–p_π–d_π conjugated systems. The data are listed in the Table.

The ^1L_a absorption maximum of phenylpentamethyldisilane at shifts to longer wavelength by 17 mμ on introduction of another pentamethyldisilanyl group at the *para*-position, whereas no bathochromic shift is observed for the *meta*-isomer. The absorption intensities of both compounds increase to a similar extent.

For a silicon atom bound to a phenyl ring, two effects have to be considered. Since it is more

TABLE

Ultraviolet spectra of some phenyl-substituted silanes in n-hexane

Compound	λ_{max} (mμ)	$\epsilon \times 10^{-4}$	Ref.
$PhSiMe_3$[a]	211·0	1·00	5
$PhSiMe_2{\cdot}SiMe_3$	231·0	1·08	2
p-$Me_3Si{\cdot}C_6H_4SiMe_3$	226·0	1·79	This work
p-$Me_3Si{\cdot}C_6H_4SiMe_2{\cdot}SiMe_3$	239·0	1·80	This work
p-$Me_3C{\cdot}C_6H_4SiMe_2{\cdot}SiMe_3$	233·0	1·86	This work
p-$Me_3Si{\cdot}SiMe_2{\cdot}C_6H_4SiMe_2{\cdot}SiMe_3$	248·0	2·45	This work
m-$Me_3Si{\cdot}SiMe_2{\cdot}C_6H_4SiMe_2{\cdot}SiMe_3$	231·0	2·44	This work

[a] In ethanol.

electropositive in nature than carbon, silicon exerts an electron-releasing inductive effect. On the other hand, because of the availability of 3*d*-orbitals, silicon has a resonance effect withdrawing electrons from the benzene ring.[4] The latter effect appears, however, not to be clear from the shifts in the ^1L_a bands of phenyl-substituted monosilanes.[5]

Previously we concluded that p_π-SiSi systems would be essential to show the effects of enhanced conjugations observed in the u.v. spectra of the phenyl- or vinyl-substituted disilanes and trisilanes.[2] In π–π^* transitions, the resonant interaction of the vacant d_π-orbitals of a silicon atom would be greater with the antibonding orbitals than with the bonding orbitals, and lowering of the d_π level by catenation of the silicon atoms would result in a more enhanced conjugation of p_π-SiSi than of p_π-Si systems.

From a consideration of the symmetries of the antibonding orbitals, only the symmetric antibonding orbital could be lowered by interactions with d_π-orbitals. This orbital would be lowered considerably further by interactions with the d_π-orbitals of both disilanyl groups in *p*-bis(pentamethyldisilanyl)benzene, while in the *meta*-isomer the effect due to the second disilanyl group should be small, as is observed experimentally.

A small bathochromic shift is observed for *p*-t-butylphenylpentamethyldisilane, indicative of the electron-withdrawing resonance effect of the pentamethyldisilanyl group.

(*Received, December* 18*th*, 1967; *Com.* 1354.)

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