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# 5,5-DIMETHYL-5*H*-DIBENZO[*b*,*f*]SILEPIN: A 14$\pi$-ELECTRON SILICON HETEROCYCLE

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## SUMMARY

5,5-Dimethyl-5*H*-dibenzo[*b*,*f*]silepin and its 10,11-dihydro-analogue have been prepared and have been studied by NMR, UV, and mass spectral techniques. The data have been evaluated on the basis of comparisons between these two new compounds themselves, and between them and known carbon analogues, with particular attention to the matter of possible Si(3$d\pi$)–C(2$p\pi$)conjugation. The results indicate ($p$–$d$)$\pi$-orbital interactions to be minimal. Mass spectral evidence gives no indication of unusual stability for the potentially "aromatic" siliconium ion derivable from the title compound.

## INTRODUCTION

Many of the distinguishing aspects of organosilicon chemistry have been attributed to the role of silicon 3*d* orbitals, and in particular, much interest has been focused on the $\pi$-interactions of these orbitals with carbon 2$p\pi$ units. Some of the earlier work has been briefly reviewed by Stone and Seyferth[1], and more recently, by Ebsworth[2].

The possiblity of Si(3$p\pi$)–C(2$p\pi$) interactions is perhaps even more intriguing. Although no such systems have been reported as yet, the generation of a siliconium ion as an integral part of a $4n+2$ $\pi$-electron silicon heterocycle offers an attractive approach. Until recently, however, no such heterocycles had been reported[3]. A new $4n+2$ $\pi$-electron silacyclic system has now been prepared, and as an initial characterization, the ($d$–$p$)$\pi$-interaction has been investigated.

It has been postulated that the vacant 3*d* orbitals on silicon may be able to provide a conjugative $\pi$-interaction with carbon 2$p\pi$ orbitals, thereby rendering $4n+2$ $\pi$-electron silicon heterocycles, *e.g.* 1*H*-silepin (I), aromatic[4], in a fashion roughly analogous to the tropylium ion (II)*. The silicon atom would then be a formally neutral participant in an aromatic system, contributing only an empty *d* orbital. It should be noted, however, that theoretical considerations, as well as some experimental

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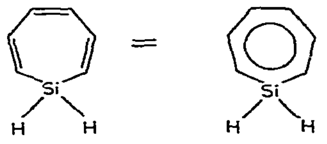
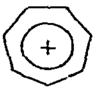
* The following distinction will be made in this paper: "($p$–$d$)$\pi$-bonding" denotes "island" or "dead-end" delocalization of carbon $\pi$-moieties into Si(3*d*) orbitals, while "$p\pi$–$d\pi$ conjugation" denotes "through" or cyclic delocalization.



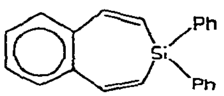
(I)



(II)

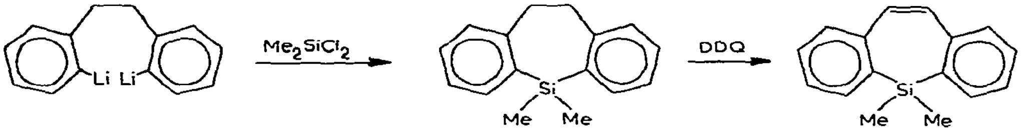
investigations, indicate that $d\pi$–$p\pi$ orbital interactions do not necessarily lead to conjugation[5,6] especially in the case of tetrahedral heteroatoms[7]. Nagy and Réffy[8] recently reported quantum mechanical calculations attributing 11% of the silicon–phenyl bonding in trimethylphenylsilane to $(p$–$d)\pi$-interaction, but denied any conjugative effects in tetraphenylsilane.

The first neutral $4n+2$ $\pi$-electron silicon heterocycle was reported by Birkofer and co-workers[3,9], who synthesized 3,3-diphenyl-3*H*-benzo[*d*]silepin (III). However, the question of $d\pi$–$p\pi$ interaction does not appear to have been addressed.



(III)

The synthesis of 5,5-dimethyl-5*H*-dibenzo[*b,f*]-silepin (V) and its 10,11-dihydro-derivative (IV) is now reported, along with the spectral evidence gathered to allow an assesment of the $\mathrm{Si}(3d\pi)$–$\mathrm{C}(2p\pi)$ interaction.



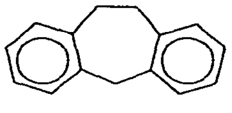
(IV) (V)

If there are any properties of (V) which may depend on the special nature of a $4n+2$ $\pi$-system, these may be more easily discerned in a comparison of (IV) and (V) than in a comparison of (III) with its tetrahydro-precursor; in the latter case, the situation is complicated by the introduction of new sites of unsaturation adjacent to silicon.

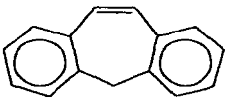
## RESULTS AND DISCUSSION

Cogent ESR evidence has been offered as proof of the ability of silyl-substituents to delocalize the odd electron in aromatic radical anions via a $d$–$\pi^*$ interaction; and in addition, ESR data have been presented as substantiation of electron withdrawal by silicon by means of $(p$–$d)\pi$-bonding in arylsilanes[10]. Curtis and Allred[11] have even offered a calculated carbon–silicon $\pi$-bond order of 0.18 in a study of Group IV-substituted biphenyl anion radicals. Corroborative UV information has also been presented in support of $p\pi$–$d\pi$ effects in compounds of phenyl-bearing elements of the higher periods of Groups IV to VI, although there is some disagreement concerning the extent of interaction[12–14].

Jaffé[12] has pointed out that heteroatoms bearing no unshared electron pairs produce only minor perturbations in a phenyl nucleus, and Brown and Prescott[13] noted the close similarity between the UV spectra of silyl- and alkylbenzenes. Both points appear to be well demonstrated by comparisons between compounds (IV) and (V) and the hydrocarbons (VI)[15] and (VII)[16,17] (Fig. 1 and Table 1)



(VI)



(VII)

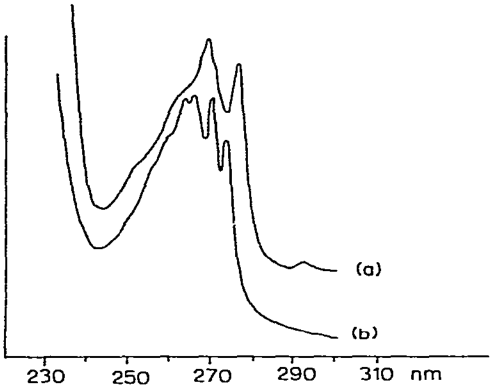


Fig. 1. UV-absorption spectra for compounds (IV) (spectrum a) and (VI) (spectrum b) in methanol. (Vertical placement is arbitrary.)

TABLE 1

UV-ABSORPTION DATA FOR COMPOUNDS (IV), (V), (VI) AND (VII)

| Compound | Solvent | λ max (nm) | λ min (nm) | ε |
|---|---|---|---|---|
| (IV) | MeOH | 269 | | 1036 |
| | | 277 | | 913 |
| | | 292 | | 75 |
| (V) | EtOH | 291 | | 10530 |
| | | | 252 | 3210 |
| (VI) | MeOH | 263 | | 872 |
| | | 266 | | 884 |
| | | 269.5 | | 876 |
| | | 273 | | 729 |
| (VII) | EtOH | 284 | | 10960 |
| | | | 245 | 2818 |

The substitution of a dimethylsilylene group for the methylene bridge in (VI) is seen to produce only a low order bathochromic shift, accompanied by hyperchromism and a slight dampening of fine structure. While the bathochromism found in going from (VII) to (V) is more substantial (7 nm), it is perhaps no more significant. Considering the peculiar potential of the $4n+2$ $\pi$-system for extensive delocalization in the event of $p\pi$–$d\pi$ conjugation, a greater shift might be expected. Also noteworthy is the close resemblance between the featureless spectra of (V) and (VII), when compared to that of anthracene which exhibits absorptions beyond 350 nm and well resolved fine structure. Nevertheless, the red shifts may be indicative of modest resonance interactions between the benzene rings and the bridging silicon. Indeed, Goodman *et al.*[14] have interpreted hypobathochromism in disubstituted silylbenzenes as evidence of $(d\text{–}p)\pi$-bonding in terms of substituent interference effects.

Neither do the NMR data (Table 2) vindicate any view of extensive bond delocalization involving Si(3*d*) orbitals, much less the aromatization of the center ring in (V). Contrary to the expectations associated with an aromatic model, the protons at positions 10 and 11 are distinctly vinylic, and moreover, they are shifted upfield from the corresponding protons in (VII). Furthermore, the silylmethyl signal is also shifted slightly upfield relative to the same signal in (IV). These observations appear at first to be consistent with an augmented degree of "dead-end" delocalization of the carbon $\pi$-system into the Si(3*d*) orbitals in the case of (V), the $4n+2$ system. However, the smaller $^{13}C$–$^{1}H$ coupling constant for the silylmethyl groups in (IV) relative to (V) imply that there is actually greater electron density at silicon in the former*.

TABLE 2

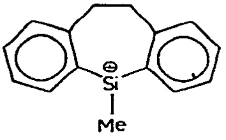
$^1H$ NMR DATA FOR COMPOUNDS (IV), (V) AND (VII)

Chemical shifts are expressed in ppm downfield relative to TMS. Coupling constants, $J(^{13}C\text{–}^{1}H)$, are expressed in Hz (experimental error, ±0.1 Hz). $CH_2Cl_2/CCl_4$ (5/95) used as solvent.

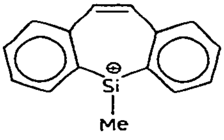
| Compound | Conc. (mg/ml) | $\delta(SiMe_2)$ | $\delta[H(10)]$and $\delta[H(11)]$ | $J(^{13}C\text{–}^{1}H)$ |
|---|---|---|---|---|
| (IV) | 16 | 0.53 | 3.16 | 119.8 |
| | 46 | 0.56 | 3.19 | |
| (V) | 18.4 | 0.49 | 6.91 | 120.2 |
| | 44 | 0.50 | 6.92 | |
| (VII) | [a] | | 6.97 | |

[a] Not reported.

The mass spectral data obtained for a mixture of (IV) and (V) may also be interpreted to indicate a smaller degree of $(p\text{–}d)\pi$-bonding in (V) relative to (IV). (Table 3) The $P-15$ (loss of methyl) peaks for both (IV) and (V) are the two most prominent in the spectrum, and both have rather low-energy appearance potentials. These fragments may be represented by the siliconium ions (VIII) and (IX). Both



(VIII)



(IX)

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* Although there is no directly analogous data available, $J(^{13}C\text{–}^{1}H)$ has been correlated with the electronegativity of substituents on carbon[18].

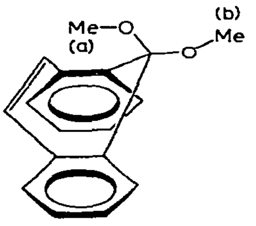
TABLE 3

MASS-SPECTRAL DATA FOR COMPOUNDS (IV) AND (V)

| Compound | *m/e* | Relative intensity (70 ev) | Appearance potential (ev) |
|---|---|---|---|
| (IV) | 238 | (1) | |
| | 223 | 1.90 | 7.5 |
| (V) | 236 | (1) | |
| | 221 | 1.62 | 8.5 |

the appearance potentials for the *P*–15 ions and their abundances relative to their respective parent molecular ions, suggest upon first inspection that the ion derived from the $4n+2$ $\pi$-electron molecule is actually the less stable, an observation consonant with a smaller degree of electron donation from the aromatic rings to the silicon atom of (IX) relative to (VIII). Both of the ions may be stabilized by Si($3p\pi$)–C($2p\pi$) interactions, but the data certainly do not lead to the expectation of augmented stability for the potentially "aromatic" siliconium ion derivable from (V).

Tochtermann *et al.*[19] have reported the NMR-nonequivalence of the two sets of methoxy protons in 1,1-dimethoxy-5*H*-dibenzo[*b*,*f*]cycloheptene (X).



At −5°: (a) δ = 7.34 ppm;
(b) δ = 6.50 ppm.

(X)

The low temperature spectra (60 MHz, $^1$H NMR) of (IV) and (V) were obtained, but as low as −94°, no splitting of the silylmethyl signals was observed. (However, some broadening of all the peaks in the spectrum did occur.) Three alternatives exist: (1), the molecules are planar; (2), the center rings in (IV) and (V) are puckered, but the difference in chemical shifts is very small; (3), the center rings are puckered, and the energetic barrier to ring inversion is quite small. The first possibility may well be discarded, as it is improbable that the center ring in (IV), containing three tetrahedral junctures, will be planar. In addition, the planarity of (V) is also thought to be unlikely.

The apparently minor differences in the nature and degree of ($p$–$d$)$\pi$-bonding interactions which are evident in the spectral properties of (IV) and (V) are perhaps surprising. The geometry of the two molecules could be expected to be substantially different in view of the greater flexibility of the seven membered ring in (IV) to be anticipated with three saturated centers. A difference in geometry could substantially affect NMR chemical shifts due to the anisotropic environment generated by the aromatic rings and the double bond in (V). Indeed, the difference in chemical shift of the two sets of methoxy protons in (X) is 0.84 ppm. Differences in the geometries of

(IV) and (V) could also be expected to influence $(p\text{-}d)\pi$-overlap between the rings and the silicon atoms, and hence the electron density at silicon. A further difference might be expected, in that the introduction of the double bond in (V) should seriously perturb the molecular orbitals of the aromatic rings, lowering the energies of some molecular orbitals thought to be major contributors to $(p\text{-}d)\pi$-bonding, thereby increasing the energy difference between the MO's and the silicon $3d$ orbitals. Should any or all of these effects be operating, they are evidently producing no gross spectral differences.

## EXPERIMENTAL

### *Spectra*

$^1$H NMR spectra were obtained with a Varian A-60A and a Varian HA-100; 60 MHz spectra were run in $CCl_4$ with TMS as internal standard, and 100 MHz spectra were run in $CH_2Cl_2/CCl_4$ 5/95 (v/v). UV spectra were recorded over the range 200 nm to 350 nm, using a Cary 14. The mass spectral data were measured on a Varian M-66, calibrated with toluene as a standard for appearance potentials.

### *5,5-Dimethyl-10,11-dihydro-5H-dibenzo[b,f]silepin (IV)*

(IV) was formed by the reaction of *o,o'*-dilithiobibenzyl with dimethyldichlorosilane in ethyl ether. The preparation of *o,o'*-dilithiobibenzyl starting from *o*-bromotoluene is according to Letsinger and Skoog[20]. And the procedure for the synthesis of the silepin parallels one employed by Kuivila and Beumel in the synthesis of 5,5-diphenyl-10,11-dihydro-5*H*-dibenzo[*b,f*]stannepin[21]. After work-up, the crude product was obtained as a yellow oil wich was then fractionally distilled under vacuum through an annular teflon spinning band column. Pure 5,5-dimethyl-10,11-dihydro-5*H*-dibenzo[*b,f*]silepin (nc) was collected at 104°–106° at 0.2 mm pressure as a colorless oil. The average yield was 16%, $n_D^{23}$ 1.5912. (Found: C, 80.49; H, 7.68. $C_{16}H_{18}Si$ calcd.: C, 80.61; H, 7.61%.)

(IV) was also successfully prepared in low yield from the reaction of dimethyldichlorosilane with the di-Grignard reagent made from *o,o'*-dichlorobibenzyl in THF[22].

### *5,5-Dimethyl-5H-dibenzo[b,f]silepin (V)*

1.5 g (0.0063 mole) of (IV) and 1.5 g (0.0066 mole) of 2,3-dichloro-5,6-dicyanobenzoquinone were placed in 25 ml toluene and refluxed for 4 days. $^1$H NMR spectrum of the crude reaction mixture indicated approximately 70% conversion. The reaction mixture was stripped of solvent on a rotary evaporator and the residue was successively chromatographed on silica gel and activated alumina columns, eluted with light petroleum. Total separation of (IV) and (V) was not achieved, but 0.3 g (23% yield) of pure 5,5-dimethyl-5*H*-dibenzo[*b,f*]silepin (nc) was obtained as a colorless oil, $n_D^{23}$ 1.6218. (Found: C, 80.97; H, 7.38. $C_{16}H_{16}Si$ calcd.: C, 81.29; H, 6.82%.)

## ACKNOWLEDGEMENT

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