

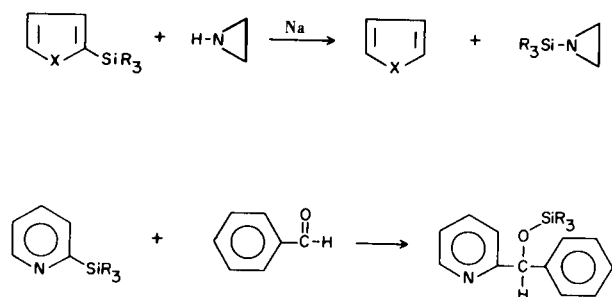
Organosilicon Compounds XI.
On (p-d) π Bonding in Silicon Substituted Furans.

Frank H. Pinkerton and Shelby F. Thames (1)

Department of Chemistry, University of Southern Mississippi

Our recent elucidation of novel silicon-carbon cleavages (Scheme A) (2,3) has prompted an investigation of the nature of the silyl-heteroaromatic bond. To this end we

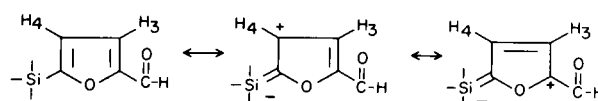
SCHEME A



have examined the NMR spectra of a variety of mono- and di-substituted furan derivatives in an attempt to uncover the presence and extent of the (p-d) π bonding interaction between the π -electron density of furan and the silicon d-orbitals.

Egorochkin, *et al.*, (4) have conducted a similar study in which nine silicon-containing furan derivatives were examined with the conclusion that (p-d) π bonding of the heterocycle to silicon influenced the chemical shift of the aromatic protons. It is worthy of note, however, that we have extended this investigation to include a wider variety of substituents on the furan moiety and that several of our chemical shift values do not agree with those reported (4).

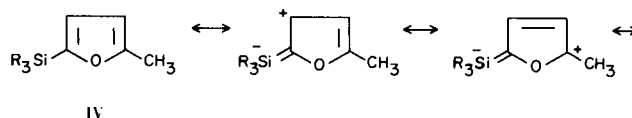
Moreover, we have clearly established that the simultaneously operative, yet opposing, +I and -M forces of the trimethylsilyl moiety are indeed present. For instance, a comparison of the chemical shifts for H₃ of XI and XII (Table I) clearly verifies that in the latter, proton shielding is affected by the trimethylsilyl group, while H₄ is shifted to lower fields. The acceptance of this seemingly contradictory effect can be rationalized by examination of the following resonance forms. It is noted that H₄ undergoes



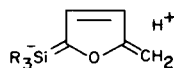
XII

electron depletion by the -M effect and thus a shift to a lower field, while H₃ remains essentially unchanged by this effect yet would be subject to the +I effect of the trimethylsilyl moiety and thus a shift to higher fields. Still another example of this combined effect is clearly documented in that H₄ and H₃ of V are strongly deshielded as compared to H₄ and H₃ of II, yet are shielded in comparison to H₄ of I. The validity of such resonance forms is given added weight when it is noted that electron depletion of I is operative on both H₄ and H₂, while H₃ remains essentially unchanged from that of II.

The combined effect of induction to the ring by methyl and (p-d) π depletion by silicon is portrayed by a comparison of IV and III. H₃, the proton least influenced by -M effects yet quite susceptible to +I effects by a common methyl moiety, is shown to remain essentially unaltered, while H₄ is shifted to lower fields in IV as a result of the -M effect of the adjacent trimethylsilyl moiety. Moreover, a small but finite shift to lower fields by virtue of -M is experienced by the methyl moiety of IV. A similar effect



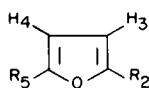
IV



is noted for the aldehydic hydrogen of XII.

The influence of (p-d) π bonding alone is apparent in comparing the H₄ shifts of VII and VIII, and IX and X where the silyl substituent affects electron withdrawal from the aromatic system. However, this withdrawal is shown to be ineffectively transmitted through the 2-

TABLE I



Compound	Substituent		Chemical Shift (δ) at Infinite Dilution			
	R ₅	R ₂	R ₅	H ₄	H ₃	R ₂
I (a)	-SiMe ₃	H	0.22	6.58	6.25	7.51
II (a)	H	H	7.31	6.26	6.26	7.31
III (a)	H	-CH ₃	7.16	6.13	5.83	2.20
IV (a)	-SiMe ₃	-CH ₃	0.20	6.44	5.83	2.24
V (a)	-SiMe ₃	-SiMe ₃	0.21	6.51	6.51	0.21
VI (a)		H	(SiMe ₂) 0.46	6.62	6.26	7.52
VII (a)	H	-COOC ₂ H ₅	7.47	6.38	7.05	(-CH ₂ -) 4.27
VIII (a)	-SiMe ₃	-COOC ₂ H ₅	0.28	6.61	7.02	(-CH ₂ -) 4.27
IX (a)	H	-CH(OC ₂ H ₅) ₂	7.26	6.19	6.32	(-CH) 5.48
X (a)	-SiMe ₃	-CH(OC ₂ H ₅) ₂	0.21	6.49	6.31	(-CH) 5.49
XI (b)	H	-CHO	7.66	6.57	7.15	(-CH) 9.66
XII (b)	-SiMe ₃	-CHO	0.31	6.68	7.09	(-CH) 9.69

(a) Cyclohexane solvent with TMS as internal reference. (b) Solvent used here was carbon tetrachloride.

TABLE II

Substituent	Compound	H ₄	ΔH_4	H ₃	ΔH_3
Aldehyde	XI	6.57	0.11	7.15	-0.06
	XII	6.68		7.09	
Ester	VII	6.38	0.23	7.05	-0.03
	VIII	6.61		7.02	
Acetal	IX	6.19	0.30	6.32	-0.01
	X	6.49		6.31	

carboxyl and 2-acetal moieties, as VIII and X show no or insignificant alterations in absorption of the methylene hydrogens and the C-H of the acetal.

Vignollet and Maire (5) have indicated that the extent of (p-d) π bonding in *para*-substituted trimethylsilyl benzenes is greatly dependent upon the electronic nature of the ring substituent. That this tenet should be expanded to include heterocycles is confirmed in the present study by examination of the differences in H₄ and H₃ for VII and VIII, IX and X, and XI and XII in Table II. The withdrawal ability of these substituents has been categorized (6) in the order aldehyde > ester > acetal. Correspondingly, the extent of the (p-d) π withdrawal between the trimethylsilyl substituent and the appropriately substituted furan ring follows the order ΔH_4 acetal

> ester > aldehyde, while the H₃ proton mirrors the accompanying inductive donation of the trimethylsilyl group in the order ΔH_3 aldehyde > ester > acetal. Thus, the greater the withdrawing ability of the "aromatic substituent," the less effective will be the (p-d) π bonding of the trimethylsilyl group owing to the diminished electron density of the furan ring, and the stronger will be the inductive donation of the silyl moiety.

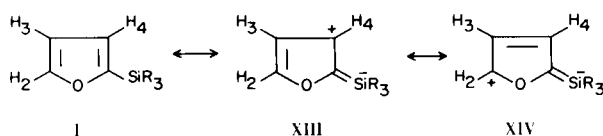
An interesting result emerges by comparison of the chemical shift of I and VII. The ester moiety is known to be both inductive and mesomeric withdrawing (-I, -M), while the silyl moiety is proposed to be inductively donating and mesomeric withdrawing (+I, -M) (Table III). Such a tenet is substantiated in that proton deshielding of H₃ is large in VII, while this effect is much less for the corresponding H₄ of I. Likewise, the importance of the (p-d) π bonding mesomeric effect of the silyl moiety is exemplified in that ΔH_2 of I is larger than ΔH_5 of VII. The +I effect of the trimethylsilyl group is confirmed by noting that ΔH_3 of I is much less than ΔH_4 of VII. Care must be taken in attempting a similar comparison between I and XII due to the change of solvent noted in Table I.

In summary, this investigation substantiates the conclusions (4) that (p-d) π bonding influences predominate in 2- and 5-trimethylsilyl substituted furans. The over-

TABLE III

Compound	Chemical Shift (δ)			Difference from Furan		
	H ₄	H ₃	H ₂	ΔH_4	ΔH_3	ΔH_2
Furan (II)	6.26	6.26	7.31			
5-Trimethylsilylfuran (I)	6.58	6.25	7.51	0.32	-0.01	0.20
	H ₃	H ₄	H ₅	ΔH_3	ΔH_4	ΔH_5
Furan (II)	6.26	6.26	7.31			
Ethyl 2-furoate (VII)	7.05	6.38	7.47	0.79	0.12	0.16

riding withdrawal effect on H₂ and H₄ suggests the significance of resonance structures such as XIII and XIV in explaining the electronic distribution within these species. Moreover, mesomeric influences can be differentiated from those of induction in that mesomeric effects on H₂ and H₄ of I are subject to the most severe chemical shifts



while H₃ is relatively immune to silicon substitution. In addition, this study adds new impetus to the argument that the extent of (p-d) π bonding is affected by the electronic nature of the accompanying ring substituent. Preliminary results indicate a similar intriguing pattern for silicon substituted thiophene, *N*-methylpyrrole and pyridine, and it is felt that a relationship between the extent of (p-d) π bonding and the resonance energy of the aromatic system may be forthcoming.

EXPERIMENTAL

The herein reported NMR spectra were obtained from a Varian A-60D spectrometer utilizing TMS as the internal standard and cyclohexane as solvent except in the case of XI and XII which are reported using carbon tetrachloride. Variations in the solvent concentrations ranging from 10% to 90% with subsequent extrapolation to infinite dilution serve to minimize the solute-solute interactions and to provide more meaningful data.

The furan (II), 2-methylfuran (III), and 2-furfural (XI) employed were obtained commercially. 2-Trimethylsilylfuran (I), bis-2,5-trimethylsilylfuran (V), di-(2-furyl)dimethylsilane (VI), and 5-trimethylsilyl-2-methylfuran (IV) were prepared according to the procedures of Lukevits and Voronkov (7,8). 2-Furfuraldiethylacetal (IX), 5-trimethylsilyl-2-furfuraldiethylacetal (X) and 5-trimethylsilyl-2-furfural (XII) were synthesized according to the procedures of Thames and Odom (9).

Ethyl 2-Furoate (VII).

Furan (34 g., 0.5 mole) in 100 ml. of anhydrous ether was metalated with *n*-butyllithium (222.2 ml.; 2.25 *M*) at 5° and allowed to stir for ½ hour, after which time the 2-lithiofuran was added dropwise to ethyl chloroformate (60 g., 0.55 mole) dissolved in 200 ml. of anhydrous ether at -70°. The resulting mixture was allowed to reach ambient temperature, at which time the lithium chloride was filtered, the solution concentrated *in vacuo*, and the residue distilled to afford 42.8 g. (61.2%) of VII boiling at 96°/24 mm., $n_D^{26} = 1.4745$; lit. (10) b.p. = 90°/15 mm.

Ethyl 5-Trimethylsilyl-2-furoate (VIII).

The metalation and subsequent condensation procedure described for VII was utilized in the preparation of VIII.

2-Trimethylsilylfuran (19.8 g., 0.14 mole) in 100 ml. of anhydrous ether was metalated with *n*-butyllithium (87.5 ml., 1.6 *M*) and the 5-lithio-2-trimethylsilylfuran condensed with ethyl chloroformate (21.7 g., 0.2 mole) at -70° to afford 17.5 g. (58.9%) of VIII boiling at 123°/23 mm., $n_D^{25} = 1.4765$.

Anal. Calcd. for C₁₀H₁₆O₃Si: C, 56.56; H, 7.61. Found: C, 56.76; H, 7.53.

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- (1) To whom correspondence should be addressed. This investigation was supported by the Mississippi Research and Development Center, Jackson, Mississippi. We are grateful to C. E. Turner and P. L. Kelly for assistance in the preparation of several of the derivatives reported herein and especially to W. H. Daudt of Dow Corning Corp. for generous supplies of many organosilicon reagents.
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Hattiesburg, Mississippi 39401