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Ultraviolet photoelectron spectroscopy and quantum-mechanical study of alkyl- and trimethylsilyl-furanes

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Abstract

Methyl-, t-butyl- and trimethylsilylfuranes have been prepared and investigated by UV photoelectron spectroscopy and CNDO/S quantum-chemical calculations. The alkyl substituents show systematic $+I$ and hyperconjugative effects. The spectra of trimethylsilylfuranes indicate that the Me_3Si has a $-M$ effect, but this is smaller than in the corresponding thiophene derivatives.

Introduction

Although the UV photoelectron spectrum of furan has been extensively investigated [1–5] the assignment of the bands is not clear. The first two bands are derived from π type orbitals. Quantum-mechanical calculations [6] and the intensities of Rydberg bands [1] indicate that the HOMO level is of a_2 symmetry. The position of the innermost π band is doubtful; neither PIES [4] and angular distribution measurement of the emitted electrons [2] nor a study of the relative intensities of He(I) and He(II) photoelectron spectra [5] have given unambiguous information on this point.

There has been only a small number of studies on substituted furans [7–11]. Usually α-substituted furans have been investigated, and only the first two orbitals considered and interpreted by HMO and IEHMO methods [8,10].

In our earlier work [6,12,13] we studied the photoelectron (PES) and Penning electron spectra of alkyl- and trimethylsilyl-thiophenes and we now present results of a study of the photoelectron spectra of methyl-, t-butyl- and trimethylsilyl-furanes. The aim of the work was to investigate the molecular electronic structure of 2- and 2,5-disubstituted furans and the substituent effect of methyl (Me), t-butyl (TB) and trimethylsilyl (TS) groups. A comparison is made with the results for thiophene derivatives. Some of the compounds investigated were studied recently by Zykov and coworkers [14], but the published spectra were of poor quality and the

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controversial conclusions they drew from CNDO/2 calculations justify a reinvestigation.

2-Trimethylsilylfuran (with some other furan and thiophene derivatives) has been studied previously by ETS and UPS [11]. It can be seen from the spectra that the empty orbitals of the substituents do not significantly stabilize the filled ring orbitals, but they do mix significantly with the unoccupied π^* orbitals. It can be concluded from earlier CT studies [15] and investigations of NMR spectra of various silicon-containing furans that $(p-d)\pi$ bonding of the heterocycle to silicon is considerable [16,17].

Experimental

UV photoelectron spectra were recorded by a double pass CMA [18] using He(I) resonance line. FWHM of Ar $^2P_{3/2}$ was 40 meV, the spectra were calibrated with N_2 and MeI.

Quantum chemical calculations were carried out by HAM/3 [19] (for methyl compounds) and modified [20] CNDO/S (for Me, TB, TS compounds) methods. The parameters used for CNDO/S calculations have been published previously. The geometries of the molecules were taken from ref. 21. The compounds were prepared by published methods [22], and their purities checked by GLC.

Results and discussion

Figure 1 shows the He(I) photoelectron spectra of the investigated compounds. The assignment of the first two bands is unambiguous for the alkyl derivatives. In the spectra of trimethylsilylfurans the fine structure of the bands has disappeared and there is a new broad band between 10.3 and 11.3 eV, but the $\pi_3(a_2)$ and $\pi_2(b_1)$ bands can easily be recognised. For further analysis of bands, CNDO/S and HAM/3 quantum chemical calculations were carried out. Table 1 shows the observed ionization potentials together with the calculated values. In our previous investigations [12,20] a linear correlation formula $IP_i = -0.74\epsilon_i + 1.70$ eV (where ϵ_i is the orbital energy) was found to give good agreement with experimental data. The calculated values in Table 1 have been corrected by use of this formula. For silyl compounds calculations were carried out with (CNDO/Sd) and without d orbitals (CNDO/S). Table 1 shows that there is no substantial difference between the results obtained by the two methods except for the well-known general stabilizing effect of d orbitals. The results of calculations, and also of other data for TS-substituted aromatic compounds [23], indicate that the broad bands between 10.3 and 11.3 eV originate from Si–C bonds. This spectral region is related to three orbitals for compound VI and six for compound VII. The lowest energy orbital corresponds to the Si–C_{Ar} bond in both cases.

The spectral region between 12 and 16 eV is very complicated, and the assignment is uncertain even for the parent compound. However it is likely that this area is related to four or five orbitals of the aromatic ring, among them the innermost $\pi_1(b_1)$ orbitals. According to the calculations the order of increasing orbital energy is a_1, b_2, a_1, $b_1(\pi)$, b_2. (It should be mentioned that earlier calculations [24–26] for furan gave a different orbital sequence.) In the substituted derivatives these bands are mixed with the bands of the substituents, causing not only band shifts but also

(Continued on p. 179)

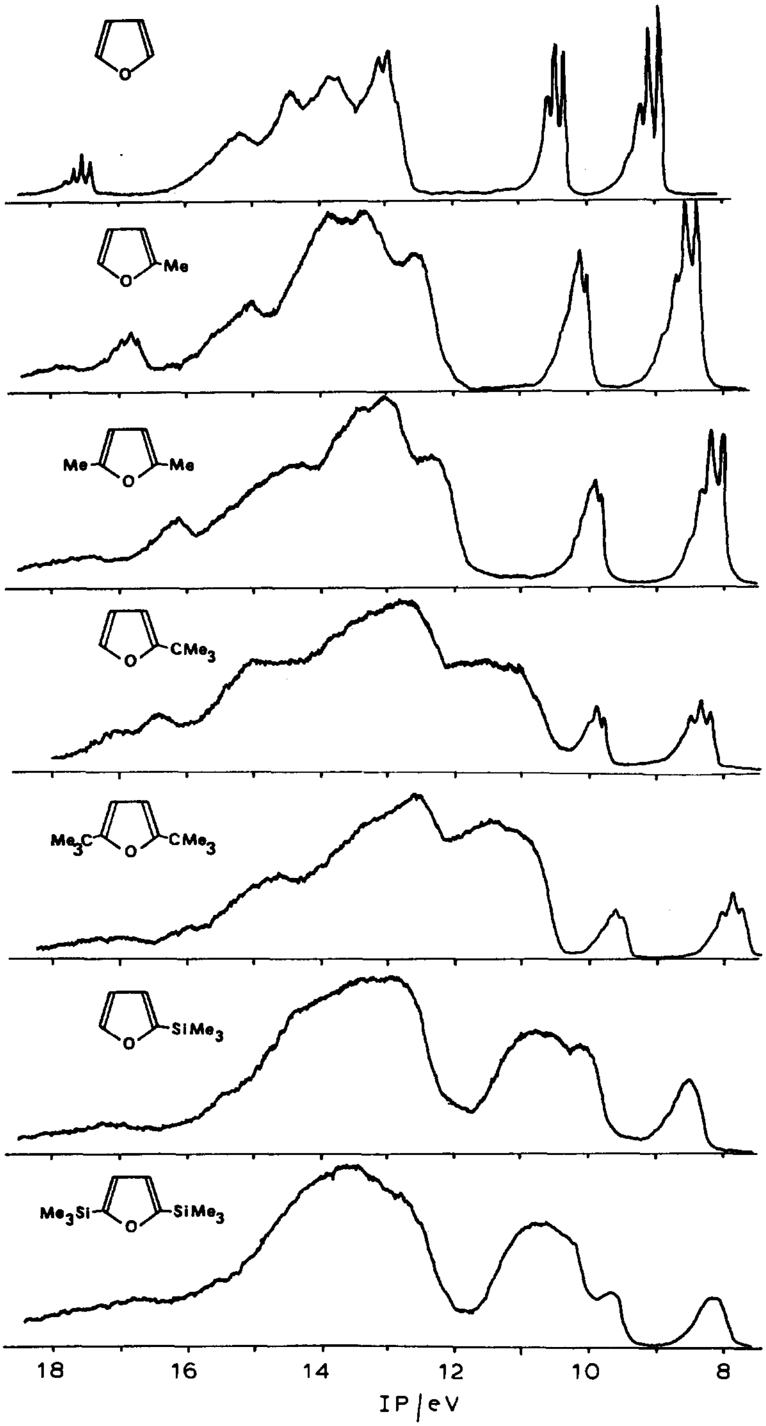


Fig. 1. He(I) photoelectron spectra of alkyl- and trimethylsilyl-furans.

Table 1

Calculated and observed ionisation potentials (in eV)

Furan (I)			2-Methylfuran (II)			2,5-Dimethylfuran (III)		
Exp.	CNDO/S	HAM/3	Exp.	CNDO/S	HAM/3	Exp.	CNDO/S	HAM/3
8.88	8.53	9.42 a_2 (π)	8.38	8.34	8.85	8.03	8.14	8.40 a_2 (π)
10.31	9.99	10.71 b_1 (π)	10.03	10.03	10.27	9.81	10.00	9.93 b_1 (π)
12.63	12.87	13.19 a_1 (n)	12.52	12.68	12.67	12.37	12.54	12.32 a_1 (n_0)
13.70	13.34	14.53 b_2	13.30	13.16	13.49 Me	13.05	12.72	12.80 b_2
14.35	13.41	14.70 a_1		13.39	13.63 Me,		13.32	13.13 b_1 (Me)
15.1	14.78	15.52 b_1 (π)	13.5–14.5	14.39	13.67 Me	13.5	13.92	13.38 b_2 (Me)
15.6	15.59	15.74 b_2		14.41	14.34		13.98	13.52 a_1 (Me)
17.3	19.79	17.07 a_1	15.0–16.55	16.01	15.08	13.8	15.24	13.82 a_2 (Me)
19.0	20.96	18.80 a_1		16.55	15.33		15.92	14.12 a_1
			16.89	19.10	16.21	14.2–15.4	15.98	14.62 a_1
			17.8	19.90	17.71		16.83	14.95 b_2
						16.1	17.92	15.20 b_1 (π)
						17.4	20.04	17.34 a_1

2-TB-furan (IV)		2,5-di-TB-furan (V)		2-TS-furan (VI)			2,5-di-TS-furan (VII)		
Exp.	CNDO/S	Exp.	CNDO/S	Exp.	CNDO/S	CNDO/S*d*	Exp.	CNDO/S	CNDO/S*d*
8.19	8.21	7.66	7.89 a_2 (π)	8.44	8.33	8.47	8.16	8.13	8.36 a_2 (π)
9.84	9.90	9.54	9.78 b_1 (π)	9.94	9.90	9.95	9.67	9.79	9.89 b_1 (π)
	11.70 C–TB		11.41 b_2 (C–TB)		10.67	11.10 C–Si		10.38	10.48 b_2
10.7–12.3	12.00 TB	10.7–12.0	11.77 a_1 (C–TB)	10.2–11.5	11.06	11.62 C–Si		10.75	10.90 a_1
	12.30 TB		11.90 a_1 (TB)		11.27	11.77 C–Si	10.0–11.5	10.99	11.08 b_2 Si–C
	12.85 n_0		12.00 b_2 (TB)		12.88	12.97 n_0		11.11	11.19 a_1
	12.97 TB		12.27 b_1 (TB)		13.28	13.39		11.15	11.21 b_1
12.3–14.0	13.13		12.28 a_2 (TB)		14.17	14.20		11.30	11.33 b_2
	13.83 TB,	12.3–14.0	12.86 a_1 (TB)	12.5–15	14.45	14.28		12.90	13.00 a_1 (n)
	14.04 TB,		12.94 b_2 (TB)		14.51	14.46	12.3–15	14.06	14.16 a_1
			13.02 a_1 (n)		15.16	15.14		14.09	14.19 a_1
			13.44 b_1 (π)		15.46	15.67 Me		14.34	14.35 b_1 (π)
			13.65 b_2		15.64	15.86 Me		14.42	14.36 b_2 (Me)
			13.75 a_1					14.42	14.36 b_1 (Me)

changes in the relative intensities of the peaks. The bands are broadened, and in the case of TS substituent the whole region consists of a single structureless broad band.

Features of the spectra are well interpreted by the calculations. The CNDO/S and HAM/3 calculations give very good values for the ionization potentials, but the shifts of the $\pi_2(b_1)$ orbitals is much better interpreted by HAM/3. A similar failure was encountered in e.g., CNDO/S calculations on thiophene derivatives or substituted benzenes [12,27]. Because of the different symmetries of the π_2 and π_3 orbitals the position of nodal surfaces is different, and therefore the effect of substituent is also different for the relevant orbitals: one of them is generally shifted much more than the other, but the CNDO/S method overestimates this effect, though the numerical values are better than in HAM/3.

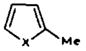
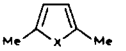
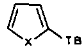
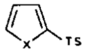
Both methods give good estimates of the positions and shifts of the ring σ orbitals between 11 and 16 eV. In methyl derivatives two sections of this region show new bands, one at 13 to 14 eV and the other at about 15 eV. The calculated ionization potentials related to methyl groups are too high by the CNDO/S method and too low by HAM/3. The innermost $\pi_1(b_1)$ orbital in the case of the parent molecule is situated at 15.1 eV in agreement with other theoretical and experimental assessments [4,25,26]. In substituted derivatives it combines with the substituent orbitals of appropriate symmetry to give two or three split MO's. This is the reason why the two methods give different estimates of the shift of π_1 orbitals. Some investigations [2] assign the peak of furan at 17.32 eV as a π_1 band, but the large shift from furan to dimethylfuran indicates that this band is of $\sigma(a_1)$ type, in accord with our calculations.

Table 2 shows the splitting of the π_3 and π_2 orbitals as well as the tendency for splitting on substitution. Δ denotes the difference in the splitting between the substituted and parent compounds, and is characteristic of the mesomeric effect of the substituent [13] The data can be compared with those of thiophene derivatives; although π_3-π_2 is very different in thiophenes and furans, the change in splitting is rather similar. In alkyl substituted compounds Δ has clearly positive value and increases upon a second substitution.

These features can be explained in terms of the hyperconjugation of alkyl groups. The opposite effect is observed with TS compounds; the Δ value is much lower, and in thiophene derivatives it is negative. This indicates that the $-M$ (d orbital) effect is nearly the same as the $+M$ (hyperconjugation) effect. In the case of furans, the $+M$ effect seems to be slightly larger, while for thiophenes the d orbital effect is more pronounced.

Table 2

Comparison of the first two π bands of furans and thiophenes

								
X = O	$\pi_3-\pi_2$ [a]	1.43	1.65	1.78	1.67	1.88	1.50	1.51
	Δ	—	0.22	0.35	0.24	0.45	0.07	0.08
X = S	$\pi_3-\pi_2$	0.65	0.80	0.97	0.78	0.90	0.54	0.50
	Δ	—	0.15	0.32	0.13	0.25	-0.11	-0.15

[a] $\Delta = (\pi_3\text{-}\pi_2)_{\text{subst.}} - (\pi_3\text{-}\pi_2)_{\text{parent}}$.

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