PHOTOELECTRON SPECTRA OF UNSATURATED OXIDES
II. 2,5-DIHYDROFURAN DERIVATIVES

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Photoelectron spectra and STO-3G calculations for 2,5-di-hydrofuran and two related compounds are reported. These results, in conjunction with the deductions drawn from localized STO-3G orbital matrix elements, confirm that the interaction between the oxygen lone pair orbital(s) and the double bond π-orbital in the compounds studied is "through bond" in nature.

In the preceding contribution [1] the photoelectron spectra of some unsaturated, cyclic oxides derived from tetrahydropyran and 1,4-dioxane have been assigned on the basis of ab initio STO-3G calculations [2]. In this communication we extend the investigation to derivatives of 2,5-dihydrofuran $\underline{2}$, namely 3,4-di-

methyl-2,5-dihydrofuran $\underline{3}$ and 3,7-dioxabicyclo[3.3.0]oct-1(5)-
ene $\underline{4}$. Ultimately, it is our aim to develop a set of parameters
which can be used in a simple equivalent bond orbital model of
more complicated oxides.
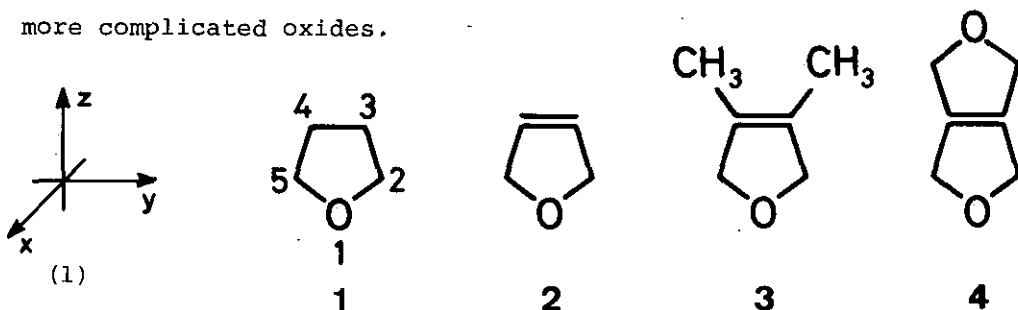
The saturated parent compound tetrahydrofuran $\underline{1}$ and the un-
saturated oxide $\underline{2}$ have been investigated first by Bain et al. [3]
and then in greater detail by Schmidt & Schweig [4] who have
shown that the previously assumed "through space" interaction be-
tween the oxygen lone pair orbital 2p(n) and the double bond π-
orbital $\pi_{3,4}$ of $\underline{2}$ [3] is small, and that their hyperconjugative
"through bond" interaction via the two methylene groups is res-
ponsible for the observed split of 1.4 eV between the bands ①
(9.18 eV) and ② (10.62 eV) in the photoelectron spectrum of $\underline{2}$.
This important conclusion, which has crucial consequences for the
nodal properties of the two canonical π-orbitals $3b_1$ and $2b_1$ of
$\underline{2}$, received strong support from other results also obtained by
Schweig et al. for 2,5-dihydrothiophene [5], methyl-substituted
1-sila- or 1-germa-cyclopent-3-ene [6] and for bicyclic oxides
[7]. Again, the work reported here is in complete agreement with
the assignment of the photoelectron spectrum of $\underline{2}$ and its ratio-
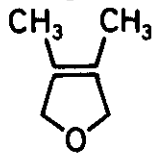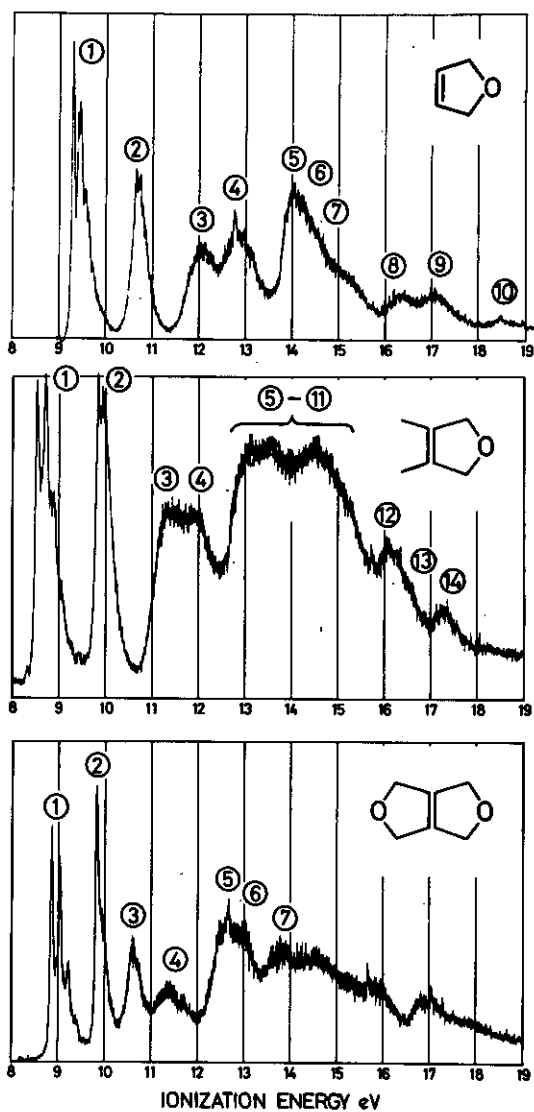nalization, as proposed by Schmidt & Schweig [4].

Figure 1

He(Iα) photoelectron spectra of 2,5-dihydrofuran (2), 3,4-dimethyl-2,5-dihydro-
furan (3) and 3,7-dioxabicyclo[3.3.0]oct-1(5)-ene (4).

Experimental Results. The He(Iα) photoelectron spectra of $\underline{2}$, $\underline{3}$ and $\underline{4}$, recorded on a modified Perkin-Elmer photoelectron spectrometer (resolution ~30 meV) and internally calibrated with rare gas mixtures, are displayed in Figure 1. The positions I_j^m of the band maxima, which are close to the vertical ionization energies I_j^v are collected in Table 1 together with the proposed assignment and the vibrational spacings of the dominant fine-structure. In the case of $\underline{2}$ the ionization energies measured previously [3][4] have been included for the sake of comparison (cf. footnote b) to Table 1).

Table 1

Ionization energies I_j^m of 2,5-dihydrofuran ($\underline{2}$), 3,4-dimethyl-2,5-dihydrofuran ($\underline{3}$) and 3,7-dioxabicyclo[3.3.0]oct-1(5)-ene ($\underline{4}$). Values in eV. Precision ±0.02 eV if two decimals given, otherwise ±0.1 eV. Precision of the vibrational spacings $\tilde{\nu}$ (cm^{-1}) is approximately ±40 cm^{-1}.

Band	Orb. (a)	I_j^m (b)	$\tilde{\nu}$	Orb. (a)	I_j^m	$\tilde{\nu}$	Orb. (c)	I_j^m	$\tilde{\nu}$
①	$3b_1$	9.18	$1420^{d)}$	$4b_1$	8.54	1480	$3b_{3u}$	8.85	1480
②	$2b_1$	10.62	560	$3b_1$	9.81	900	$2b_{2g}$	9.80	1200
③	$9a_1$	12.0		$12a_1$	11.3		$2b_{3u}$	10.6	
④	$6b_2$	12.7		$9b_2$	11.9		$6b_{1u}$	11.3	
⑤	$8a_1$	13.9		$11a_1$			$8a_g$	12.6	
⑥	$5b_2$	14.6					$4b_{3g}$	12.9	
⑦	$1a_2$	15.3					$7a_3$	13.8	

a) Assumed symmetry C_{2v}. b) Values obtained in previous work, in eV: ①, 9.14 [3], 9.16 [4]; ② 10.59 [3], 10.57 [4]. c) Assumed symmetry D_{2h}. d) Secondary vibrational spacing 1060 cm^{-1}.

STO-3G Orbital Models. The molecules $\underline{2}$, $\underline{3}$ and $\underline{4}$ were assumed
to be planar, belonging to the symmetry groups C_{2v} and D_{2h} res-
pectively. For $\underline{2}$ *this is in keeping with the conclusions reached*
by Ueda & Shimanouchi [8] *from an analysis of the ring puckering*
vibration. In agreement with their results, STO-3G calculations
[2] for $\underline{2}$ with different out-of-plane bending angles α, defined
according to the following diagram, yielded a flat potential with

$$(2)$$
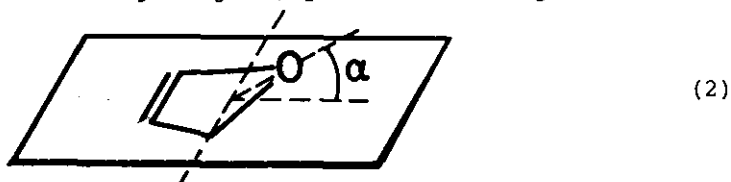
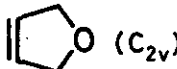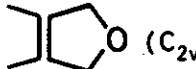a minimum for $\alpha = 0$. The same has been assumed to be true for $\underline{3}$
and $\underline{4}$. Thus, all three molecules should exhibit strict σ/π-sepa-
ration. Note that with the definitions of the axes given in (1)
the π-orbitals belong to the irreducible representations A_2 and
B_1 of C_{2v} (molecules $\underline{2}$ and $\underline{3}$) or B_{1g}, B_{2g}, A_u and B_{3u} of D_{2h}
(molecule $\underline{4}$).

The STO-3G [2] calculations were carried out using standard
bond lengths [9] throughout, and C_{2v} (for $\underline{2}$, $\underline{3}$) or D_{2h} symmetry
(for $\underline{4}$). This leads to the following structural parameters:

Bond	Length	Angle	Degrees	
$O_{(1)}-C_{(2)}$	143 pm	$O_{(1)}C_{(2)}C_{(3)}$	106.5°	
$C_{(2)}-C_{(3)}$	152 pm	$C_{(2)}C_{(3)}C_{(4)}$	109.0°	
$C_{(3)}-C_{(4)}$	134 pm	$C_{(2)}O_{(1)}C_{(5)}$	109.1°	(3)
$C_{(2)}-H$	109 pm	$HC_{(2)}H$	110°	
$C_{(3)}-H$	108 pm	$HC_{(3)}C_{(4)}$	125.5°	

Table 2

STO–3G orbital energies ϵ_j^{STO-3G} and ionization energies I_j^{STO-3G} derived from them according to (4). All values in eV.

	I$\bigcirc$O (C$_{2v}$)				$\supset$$\bigcirc$O (C$_{2v}$)				O$\diamond$O (D$_{2h}$)		
j	$-\epsilon_j^{STO-3G}$	Orb.	$I_j^{STO-3G\,a}$	$I_j^{STO-3G\,b}$	$-\epsilon_j^{STO-3G}$	Orb.	$I_j^{STO-3G\,a}$	$I_j^{STO-3G\,b}$	$-\epsilon_j^{STO-3G}$	Orb.	$I_j^{STO-3G\,a}$	$I_j^{STO-3G\,b}$
1	7.89	$3b_1$	9.57	9.08	7.25	$4b_1$	9.10	8.54	7.47	$3b_{3u}$	9.26	8.73
2	9.62	$2b_1$	10.84	10.55	9.21	$3b_1$	10.54	10.20	9.24	$2b_{2g}$	10.56	10.22
3	10.65	$9a_1$	11.60	11.41	10.22	$12a_1$	11.28	11.05	10.02	$2b_{3u}$	11.13	10.88
4	12.40	$6b_2$	12.88	12.90	11.62	$9b_2$	12.31	12.23	10.16	$6b_{1u}$	11.24	11.00
5	13.53	$8a_1$	13.71	13.85	12.29	$11a_1$	12.80	12.80	11.80	$8a_g$	12.44	12.39
6	13.90	$5b_2$	13.99	14.17	13.49	$8b_2$	13.68	13.82	12.45	$4b_{3g}$	12.92	12.94
7	14.78	$1a_2$	14.63	14.91	14.23	$2a_2$	14.23	14.44	12.83	$7a_g$	13.20	13.26
8	16.93	$1b_1$	16.21	16.73	14.26	$7b_2$	14.25	14.47	13.72	$5b_{2u}$	13.85	14.01
9	17.53	$7a_1$	16.65	17.23	14.87	$1a_2$	14.70	14.98	14.37	$3b_{3g}$	14.33	14.50
10	19.26	$4b_2$	17.93	18.69	15.04	$2b_1$	14.82	15.13	14.76	$1a_u$	14.62	14.89

a) STO–3G ionization energies scaled according to eqn. (4) with parameters from Ref. [1].

b) STO–3G ionization energies scaled according to eqn. (4) with parameters from this work.
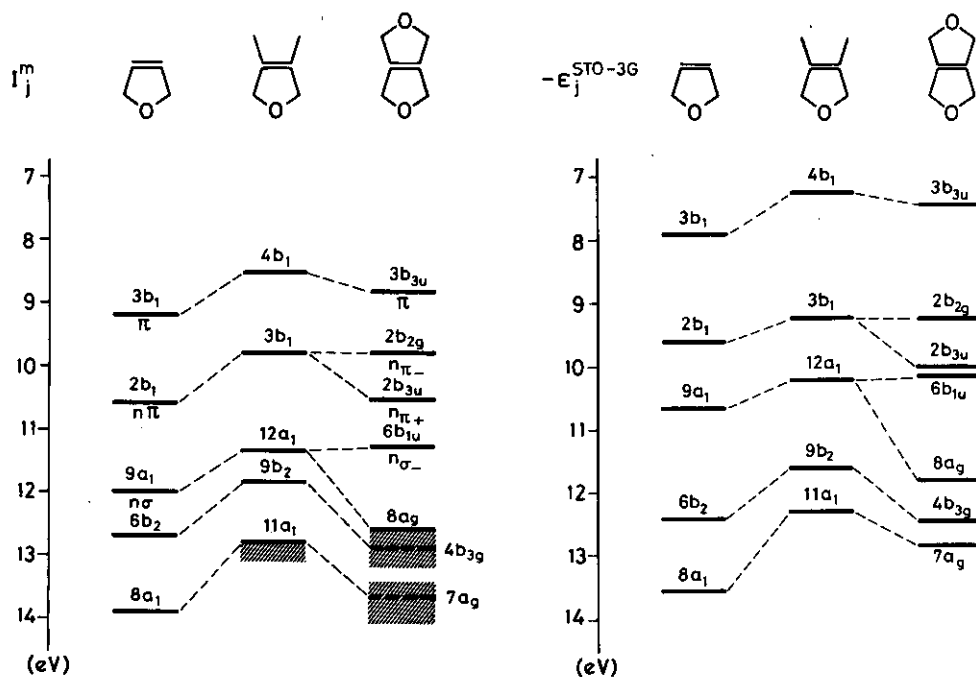
Figure 2

Correlation diagram of observed ionization energies, I_j^m, and calculated orbital energies, $-\varepsilon_j^{STO-3G}$.

For the two methyl groups in $\underline{3}$ all bond angles were taken to be tetrahedral.

The orbital energies ε_j^{STO-3G} and the symmetry assignment of the canonical orbitals are listed in Table 2 and compared to the experimental values I_j^m in the orbital correlation diagram shown in Figure 2. Clearly, the trends that occur in the observed ionization energies I_j^m are well reproduced by the calculated orbital energies ε_j^{STO-3G}.

To obtain quantitative estimates of the ionization energies, it is necessary to transform the ε_j^{STO-3G} into I_j^{STO-3G} values, using a least squares adjusted scaling function of the type

$$I_j^{STO-3G} = a + b\ \varepsilon_j^{STO-3G} \qquad\qquad (4)$$

used in the previous paper [1]. However, the parameters a and b depend on the type of molecule investigated and a calibrated relationship (4) should only be used for closely similar systems. Whereas a = 3.77 eV, b = -0.737 were the values obtained in ref. [1], the present set of data (13 degrees of freedom; correlation coefficient 0.984) yields a = 2.41 and b = -0.846, i.e. a steeper regression line. In Table 2 we give the predicted I_j^{STO-3G} values for both sets of parameters to exemplify the size of error which arises if such scaling functions are carried over from one set of compounds, i.e. 1,4-dioxin and related systems [1], to another, i.e. 2,5-dihydrofuran derivatives.

Table 3

Matrix elements for π-type localized STO-3G orbitals of unsaturated oxides. Self energies are denoted by A, 1,2-interaction and 1,3-interaction terms by B and Γ respectively. All values in eV.

Cmpd.	A_π	A_0	A_{CH_2} a	A_{CH_3} b	$B_{CH_2,0}$ a	$B_{CH_2,\pi}$ a	$B_{CH_3,\pi}$ b	$\Gamma_{0,\pi}$
<u>2</u>	-9.04	-10.98	-14.56	-	-2.33	-1.59	-	-0.36
<u>3</u>	-8.85	-10.83	-14.42	-14.49	-2.32	-1.60	-1.51	-0.37
<u>4</u>	-9.29	-11.29	-14.80	-	-2.33	-1.59	-	-0.36

a) Lower index CH_2 refers to the π-type linear combination of the two geminal localized CH orbitals.

b) Lower index CH_3 refers to the π-type component of the degenerate pair of linear combinations of the three localized CH-orbitals, which is anti-symmetric relative to the plane of the molecule.
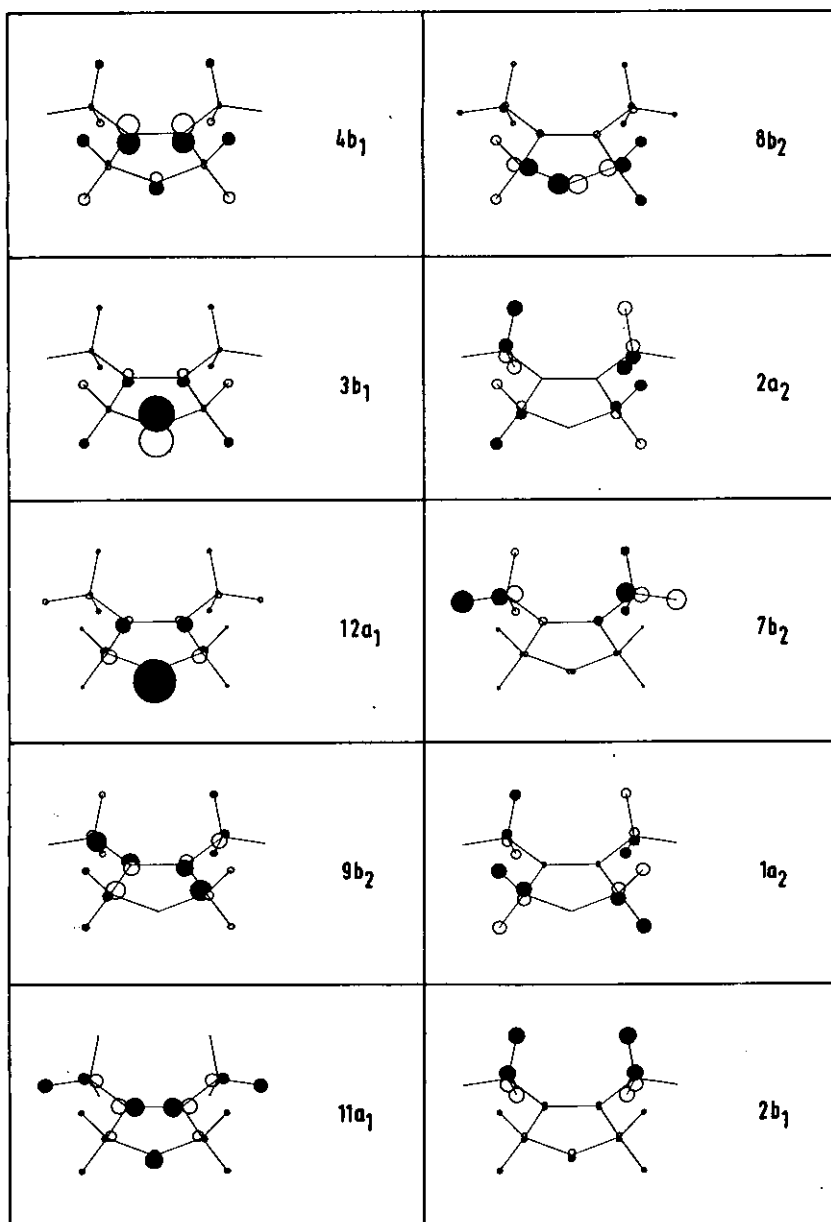
Figure 3

The ten highest occupied canonical molecular orbitals of $\underline{\underline{3}}$.

To illustrate the character of the orbitals of $\underline{2}$ and $\underline{3}$ the
ten highest occupied canonical STO-3G orbitals of $\underline{3}$ drawn by
MOPLOT [10] are graphically displayed in Figure 3. Attention is
drawn to the nodal properties of $4b_1$ and $3b_1$ which are in agree-
ment with and support the conclusions drawn by Schmidt and
Schweig [4,5].

Localized Molecular Orbitals. The STO-3G canonical orbitals
of $\underline{2}$, $\underline{3}$ and $\underline{4}$ have been transformed into localized orbitals,
using the Foster-Boys procedure [11]. For the π-type localized
orbitals of these three compounds the self energies (A), vicinal
interaction terms (B) and 1,3-interactions (Γ) between $O-2_p$
and the double bond π orbitals are collected in Table 3. As ob-
served previously [1] the self energies reflect the average elec-
tronegativity of the close evironment of the bond to which the
particular localized orbital belongs, e.g. A_π lies higher in $\underline{3}$
than in $\underline{2}$, but lower in $\underline{4}$. In contrast the 1,2-interaction terms
are reasonably constant. As expected, the transannular interaction
$\Gamma_{0,\pi}$ between the oxygen lone pair 2p-orbital and the double bond
π-orbital is small compared to B_{CH_2O} and $B_{CH_2,\pi}$ which explains
the nodal properties of the highest occupied canonical orbital in
each of the three compounds.

Discussion. On the basis of the STO-3G calculations, loca-
lized orbitals and the photoelectron spectroscopic results of
Schmidt and Schweig [4,5], there can be little doubt that trans-

annular interactions in 2,5-dihydrofurans and related systems are of secondary importance. From Figure 3 and Tables 1 and 2 band ① of the spectra (Figure 1) corresponds to electron removal from an orbital predominantly double bond-π in character. Additional support for this is found in the band shapes and vibrational spacings. Band ③ of 2 and 3 arises from π-type orbitals located primarily on oxygen. It should be noted here that shifts observed for bands ① and ② of 2 due to methyl-substitution are approximately equal, in contrast to what one would expect on the basis of first-order perturbation theory. The two combinations of π-type orbitals on oxygen are split in 4, the in-phase combination being stabilized by through bond interaction. .

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