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54. The Electronic Structure of Vinyl Ethers and Sulfides with Interrupted Conjugation Examined by Photoelectron Spectroscopy

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Summary. Photoelectron spectroscopy has been used to examine the consequences of steric inhibition of conjugation in a distorted vinyl sulfide and vinyl ether. Based upon the degree of interaction a deviation from coplanarity of 70°–75° is calculated for 9-oxabicyclo[3.3.1]non-1-ene (**3**) and approximately 75°-80° for the sulfur analog **6**.

Twisting two conjugated, individually planar π-systems R and S by an angle θ_{RS} with respect to each other produces changes in the electronic structure of the molecule R-S. Within the framework of a simple HMO-type model these changes are linked to the decrease of the crossterm,

$$\beta(\theta_{RS}) = \beta_0 \cos \theta_{RS} \tag{1}$$

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between the two atomic p-orbitals of the bond joining R to S ($\theta_{RS} = 0$ for R and S coplanar). Among other things the molecular orbital energies ε_j of R-S will change and thus, according to *Koopmans'* theorem ($I_{v,j} = -\varepsilon_j$) [1], so will the band position $I_{v,j}$ in the photoelectron (PE.) spectrum of R-S. In the particular case that both R and S are hydrocarbon π-systems, PE. spectroscopy has proved to be a useful probe for the determination of θ_{RS}, as evidenced by the results obtained for biphenyls [2], butadienes [3], phenylethylenes [4] and cyclic di- and trienes [5]. The application of
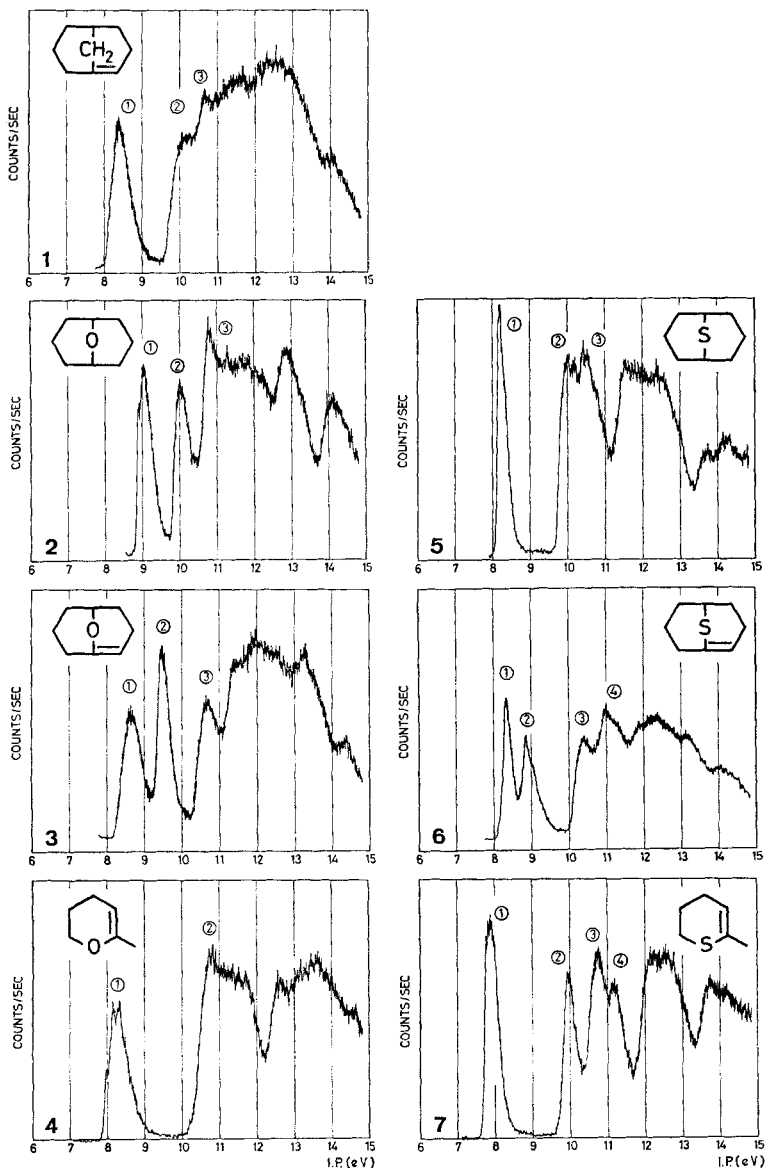

Fig. 1. *He(I) photoelectron spectra*

(1) is less straightforward if R and S are lone-pair atomic orbitals n, which may be of p, sp^3 or of an intermediate degree of hybridisation. Nevertheless, pertinent information concerning their relative conformation has been obtained by PE. spectroscopy for hydrazines [6], disulfides [7] and peroxides [8]. Although a nitrogen $2p$ lone-pair orbital n_N (in R) conjugating with an aryl π-system S has been shown amenable to this type of approach (S = phenyl [9], S = naphthyl [10]), the oxygen analogs presented 'severe limitations' due to the difficulties in assigning the PE.-spectra [9].

In vinyl ethers this problem is expected to be less serious because of the simplicity of their π-system, which consists of only two occupied molecular π-orbitals. Thus the low energy part of the corresponding PE. spectrum should exhibit well spaced and easily identifiable bands. Recent synthesis of the distorted molecule 9-oxabicyclo-[3.3.1]non-1-ene (3) [11] and of its sulfur analog 6 [12] allowed us to investigate the dependence of the π-band positions on $\theta_{RS} \equiv \theta_{\pi n_X}$, i.e. the twist angle between the oxygen or sulfur atomic lone pair p-orbital n_O or n_S and the two centre π-orbital π of the ethylene moiety.

Experimental Results. – In Fig. 1 are shown the He(I) PE. spectra of bicyclo-[3.3.1]non-1-ene (1), 9-oxabicyclo[3.3.1]nonane (2), 9-oxabicyclo[3.3.1]non-1-ene (3), 2-methyl-4,5-dihydropyran (4), 9-thiabicyclo[3.3.1]nonane (5), 9-thiabicyclo[3.3.1]-non-1-ene (6) and of 2-methyl-4,5-dihydrothiapyran (7). The spectra were obtained with a modified PS-15 PE. spectrometer (*Perkin-Elmer*, Beaconsfield, England), based
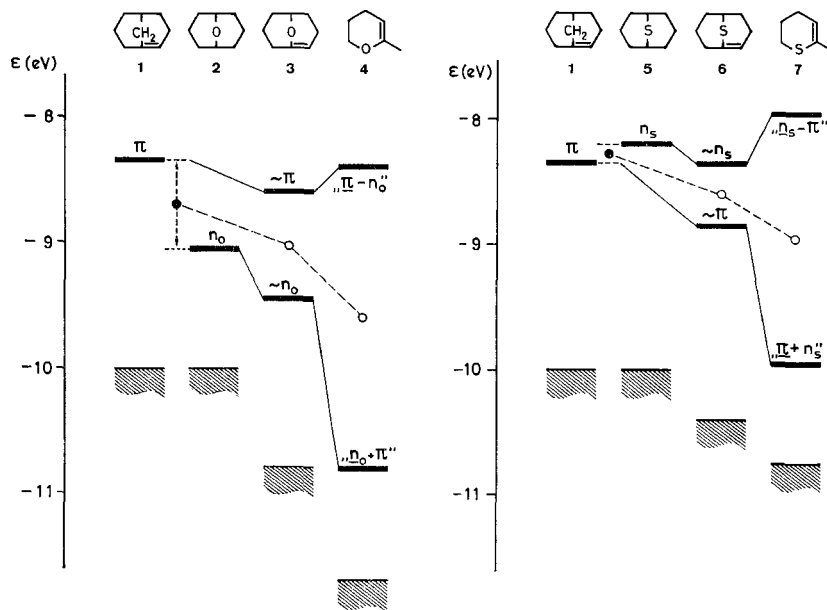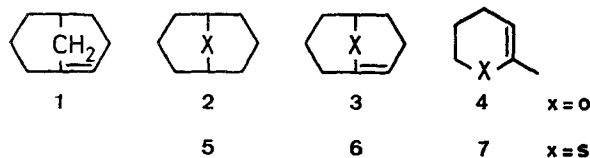

Fig. 2. *Correlation diagrams.* The 'observed' orbital energies ε_j (solid lines) are defined according to $\varepsilon_j = -I_{v,j}$. The full circles (●) correspond to the mean of $A(\pi)$ and $A(n_X)$, $X = O$, or S, the open circles (○) to the mean $\bar{\varepsilon} = (\varepsilon_1 + \varepsilon_2)/2$. In the case of 4 and 7 the underlined basis orbital (e.g. '$\underline{n}_O + \pi$' in diagram a) is that which contributes with greatest weight to the linear combination in question. The shaded area indicates the onset of the σ-band system

on the design of *Turner* [13] and calibrated by simultaneous admission of a xenon/argon gas mixture. Vertical ionization energies $I_{v,j}$ of the first three or four bands

| 1 | 2 | 3 | 4 | $X = O$ |
| | | | 5 | 6 | 7 | $X = S$ |

(approximated by the corresponding positions $I_{m,j}$ of the band maxima: $I_{v,j} \approx I_{m,j}$ are collected in Tab. 1. The 'observed' orbital energies ε_j, obtained by applying *Koopmans'* theorem in reverse $(\varepsilon_j = -I_{v,j})$ are shown in the correlation diagrams of Fig. 2.

Discussion. – The two correlation diagrams of Fig. 2 are almost self-explanatory, especially if taken in conjunction. They suggest that a discussion in terms of 'through-space' and 'through-bond' interactions [14] between the lonepair p-orbitals n_X and the two-centre π-orbital π of the double bond yield a satisfactory explanation of the 'observed' orbital pattern. On the other hand a recent investigation has revealed

Table 1. *Ionization energies* (I_v). The values given correspond to the peak maxima and are thus close to the vertical ionization energies. All values (in eV) have been rounded to the nearest 0.05 or 0.1 eV

| | | | | Molecule | | | |
Band	1	2	3	4	5	6	7
①	8.3_5	9.0_5	8.6_0	8.4_0	8.2_0	8.3_5	7.9_5
②	10.0	10.0_0	9.4_5	10.8_0	10.0_0	8.8_5	9.9_5
③	10.6_5	10.8_0	10.8		10.4_5	10.4_0	10.7_5
④						11.0	11.2

[15] that the interplay of the two types of orbital interaction mentioned above can be rather complex in bicyclic systems, such as **1, 2, 3, 5** and **6**. In addition, as far as 'through-bond' interactions are concerned, a comparison of **2** with **3** and of **5** with **6** is complicated by the fact that the saturated and unsaturated systems differ in the conformation of the σ-frame ($X = O$ or S), as shown by perspective drawings **8** and **9**.

| 8 | 9 |

For these reasons we shall rely as much as possible on simple empirical correlations of ionization energies $(I_{v,j})$, supplemented by molecular orbital rules of thumb, to rationalize the observed PE. spectra. To this end, our first task is to assign reasonable basis energies $A'(\pi)$ and $A'(n_X)$ to the localized orbitals π and $n_X(X = O$ or $S)$ of the molecules **3, 6** $(\theta_{\pi n_X} \gg 0)$ and **4, 7** $(\theta_{\pi n_X} \approx 0)$ in the following manner:

$M(\varphi)$ and $M(\phi)$ are two molecules possessing the same σ-frame but containing either the semi-localized orbital φ or ϕ as a characteristic feature, *e.g.* $M(\pi) \equiv$ **1**,

$M(n_O) \equiv 2$. We identify the negative ionization energies $I_V(\varphi)$ of $M(\varphi)$ and $I_V(\phi)$ of $M(\phi)$, which are associated with the ejection of an electron from the canonical molecular orbitals dominated by φ or ϕ, with the orbital energies $A(\varphi)$ or $A(\phi)$:

$$A(\varphi) = -I_V(\varphi) ; A(\phi) = -I_V(\phi) \tag{2}$$

Here and in the following we shall assume that $I_V(\varphi)$ and $I_V(\phi)$ are the first ionization energies of $M(\varphi)$ and $M(\phi)$ and that the corresponding bands in their PE. spectra are well separated from the following σ-band system. The presence in a molecule $M(\varphi,\varphi)$ (with same σ-frame as $M(\varphi)$) of two semi-localized orbitals φ of same type will then lead to two bands in the PE. spectrum at positions $I_{V,1}(\varphi)$ and $I_{V,2}(\varphi)$. Experience has shown that the mean energy

$$\overline{I_V(\varphi)} = (I_{V,1}(\varphi) + I_{V,2}(\varphi))/2 \tag{3}$$

usually differs from $I_V(\varphi)$ observed for $M(\varphi)$.

This means that we have to assign to the two orbitals φ in $M(\varphi,\varphi)$ a new basis energy

$$A'(\varphi) = \overline{I_V(\varphi)} \tag{4}$$

into which we have absorbed the shift $\delta A_\varphi(\varphi)$ induced in $A(\varphi)$ by the presence of the second orbital φ:

$$A'(\varphi) = A(\varphi) + \delta A_\varphi(\varphi) \tag{5}$$

For a molecule $M(\varphi,\phi)$ which contains two different semi-localized orbitals φ,ϕ we shall assume that the shift parameters $\delta A_\phi(\varphi)$ and $\delta A_\varphi(\phi)$, *i.e.* the shifts induced in $A(\varphi), [A(\phi)]$ by the presence of $\phi, [\varphi]$ are the same as $\delta A_\phi(\phi)$ and $\delta A_\varphi(\varphi)$ respectively. It follows for $M(\varphi,\phi)$:

$$\begin{aligned} A'(\varphi) &= A(\varphi) + \delta A_\phi(\phi) \\ A'(\phi) &= A(\phi) + \delta A_\varphi(\varphi) \end{aligned} \tag{6}$$

If $\varepsilon_1 = -I_{V,1}$ and $\varepsilon_2 = -I_{V,2}$ are the 'observed' *Koopmans*' orbital energies of $M(\varphi,\phi)$, a test for the validity of the crude approximation (6) is provided by the relationship

$$A'(\varphi) + A'(\phi) = \varepsilon_1 + \varepsilon_2 \tag{7}$$

which should be satisfied within reasonable limits of error.

Only if condition (7) is found to be true can we compute the crossterm

$$B_{\varphi\phi} = \langle \varphi | \mathcal{H} | \phi \rangle \tag{8}$$

for the conjugative interaction of φ and ϕ in $M(\varphi,\phi)$ from the observed split $I_{V,2} - I_{V,1} \equiv \varepsilon_1 - \varepsilon_2$ between the corresponding bands in its PE. spectrum:

$$B_{\varphi\phi}^2 = \left(\frac{\varepsilon_1 - \varepsilon_2}{2} \right)^2 - \left(\frac{A'(\varphi) - A'(\phi)}{2} \right)^2 \tag{9}$$

π-Orbitals. The π-ionization energies $I_V(\pi)$ of ethylene (10.5 eV) [16] 1-butene (1-ethylethylene) (9.6 eV) [17], 3-hexene (1,2-diethylethylene) (9.0 eV) [17] extrapolate to $I_V(\pi) = 8.4$ eV for 1,1,2-triethyl-ethylene, *i.e.* a double bond similarly

substituted as the one in **1**. The same value is obtained if the *Hammett*-type relationship for ionization energies, originally proposed by *Cocksey et al.* [18], is used in conjunction with a revised set of parameters for alkyl substituents [19]. It agrees within the limits of error with the one observed for **1**, namely $I_v(\pi) = 8.3_5$ eV. This may seem surprising because **1** belongs to the class of 'anti-*Bredt*' hydrocarbons [20] for which one would have expected a reduced $I_v(\pi)$-value, in view of the deformation which must necessarily be present in the double bond. However, it has been shown [21] that even in bicyclo[4.2.1]non-1(2)-ene (**10**) and bicyclo[4.2.1]non-1(8)-ene (**11**), for which an optimized valence force field calculation predicts

10   **11**

twist angles of 18.4° and 16.6°, respectively [22], the observed ionization energies of $I_v(\pi) = 8.4_5$ eV for **10** and 8.37 eV for **11** are those expected for a correspondingly substituted planar ethylene molecule. (Although obvious, it is worth mentioning that the orbital energy $A(\pi) = I_v(\pi) = -8.4$ eV deduced does not correspond to the self-energy of a localized π-orbital, *i.e.* the energy one would have obtained by applying a localization technique to a many-electron SCF wave function of **1**. In fact $A(\pi)$ contains all of the destabilizations due to the interactions of a truly localized π-orbital with all of the σ-orbitals of the molecule, *i.e.* $A(\pi)$ is the energy of the π-dominated canonical orbital of **1**).

The presence of a second double bond in a mono- or bicyclic diene lowers the mean π-ionization energy $\overline{I_v(\pi)}$ (see (3) with $\varphi = \pi$) relative to the ionization energy of the corresponding mono-ene by -0.2 to -0.4 eV [5], depending on the type and size of the system. This corresponds to a positive change $\delta A_\pi(\pi) = 0.2$ to 0.4 eV in the basis energy $A(\pi)$ of the π-orbitals (*cf.* (5)). In the following we shall use a mean value $\delta A_\pi(\pi) = \delta A_\pi(\varphi) = 0.3$ eV for the influence of an added double bond on the basis energy $A(\varphi)$ of a semi-localized orbital φ, under the assumption implied in (6) that this value is independent of the character of φ.

Oxygen n-*orbital.* The ionization energy associated with the ejection of an electron from an oxygen lone-pair orbital n_O decreases with increasing size of the substituting alkyl groups: $I_v(n_O) = 9.9_5$ eV, $O(Me)_2$; 9.5 eV, $O(Et)_2$; 9.3_5 eV, $O(iPr)_2$; 8.9_5 eV, $O(tBu)_2$ [18] [23]. These values agree with those found for tetrahydrofuran, $I_v(n_O) = 9.5$ eV [24] and tetrahydropyran, $I_v(n_O) = 9.5$ eV [25]. In comparison the lone-pair ionization energy $I_v(n_O) = 9.0$ eV of **2** is rather low, especially if contrasted to that of 7-oxanorbornane, $I_v(n_O) = 9.5_5$ eV [24]. (We shall comment on this below.)

Introducing a second oxygen atom into the ring system increases the mean ionization energy $\overline{I_v(n_O)}$ as defined in (3) (with $\varphi = n_O$) by 0.6 to 0.7 eV relative to $I_v(n_O)$ of the parent compound *e.g.* $\overline{I_v(n_O)} = 10.0_5$ eV for 1,4-dioxane and 10.2 eV for 1,3-dioxane relative to $I_v(n_O) = 9.5$ eV for tetrahydropyran [25]. These and similar examples suggest that $\delta A_{n_O}(\varphi) = -0.6_5$ eV is a reasonable value to use for the shift induced in $A(\varphi)$ by the presence of an additional oxygen centre in the molecule.

Sulfur n-orbital. In analogy with the results observed for the ethers, the lone-pair ionization energies $I_v(n_S)$ of the sulfides decrease with increasing size of the alkyl groups: $I_v(n_S)$ = 8.7 eV, $S(Me)_2$; 8.4 eV, $S(Et)_2$; 8.3 eV, $S(iPr)_2$; 8.1 eV, $S(tBu)_2$ [7] [26]. The values observed for tetrahydrothiophene and pentamethylene sulfide are 8.4 eV [27] and 8.5 eV [25] respectively. Again, as in the case of the oxygen analogues, the ionization energy $I_v(n_S)$ = 8.2 eV of **5** is low, in particular if compared to $I_v(n_S)$ = 8.4_5 eV found for 7-thianorbornane [28].

An increase of approximately 0.4 of the mean ionization energy $\overline{I_v(n_S)}$, (3) (with $\varphi = n_S$), is observed if a second sulfur atom is introduced, *e.g.* $I_v(n_S)$ = 8.8_5 eV for 1,4-dithiane relative to $I_v(n_S)$ = 8.4_5 eV for pentamethylene sulfide. Consequently we shall use $\delta A_{nS}(\varphi)$ = -0.4 eV for the lowering of $A(\varphi)$ induced by the presence of a sulfur atom.

To summarize: With respect to the definitions (2) to (7) we shall use the following set of shift parameters:

$$\delta A_\pi(\pi) \quad = \delta A_\pi(\varphi) \quad = -0.3 \text{ eV}$$
$$\delta A_{n_O}(n_O) = \delta A_{n_O}(\varphi) = -0.6_5 \text{ eV} \qquad (10)$$
$$\delta A_{n_S}(n_S) = \delta A_{n_S}(\varphi) \quad = -0.4 \text{ eV}$$

The adequacy of the approximation (6) together with the parameters $A(\varphi)$ given in (10) is demonstrated in Tab. 2 by the almost perfect agreement of the calculated value $\overline{A'} = (A'(\varphi) + A'(\sigma))/2$ with the 'observed' mean $\overline{\varepsilon} = (\varepsilon_1 + \varepsilon_2)/2$ of the orbital energies of the compound containing both φ and ϕ. This means that condition (7) is satisfied, in particular for the systems **3, 4, 6** and **7**.

We are now in a position to discuss the correlation diagrams of Fig. 2. With the parameters $A'(\pi)$, $A'(n_X)$ (X = O or S), ε_1 and ε_2 given in table 2 for **3, 4, 6** and **7** we calculate the crossterms $B_{\pi n_X}$ using formula (9). Because $\varepsilon_1 + \varepsilon_2$ does not equal exactly $A'(\pi) + A'(n_X)$ one could in principle make small adjustments in the latter parameters to force agreement. However, it can be shown that this does not yield significant changes in $B_{\pi n_X}$, except in the case of **3** where the uncertainty is of the order of 0.1 eV. The value of $B_{\pi n_X}$ measures the 'through-space' conjugative interaction of π and n_X (resonance integral) and has therefore been given a negative sign. We find:

$$
\begin{array}{ll}
B_{\pi n_O} & B_{\pi n_S} \\
\textbf{3: } -0.3 \text{ to } -0.4 \text{ eV} & \textbf{6: } -0.2 \text{ eV} \\
\textbf{4: } \qquad\qquad -1.2 \text{ eV} & \textbf{7: } -1.0 \text{ eV}
\end{array}
\qquad (11)
$$

This result expresses numerically what is evident by inspection from Fig. 2, namely that the direct, conjugative 'through-space' interaction between π and n_X in **4** and **7** is much larger than in **3** and **6**. If we postulate that the angles $\theta_{\pi n_X}$ in **4** (X = O) and **7** (X = S) are close to zero, *i.e.* that these molecules assume a half-chair conformation and that the dependence of $B_{\pi n_X}$ on $\theta_{\pi n_X}$ obeys (1), then the following twist angles are calculated for **3** and **6**:

$$\textbf{3: } \theta_{\pi n_O} = 70° \text{ to } 75°; \quad \textbf{6: } \theta_{\pi n_S} = 75° \text{ to } 80° \qquad (12)$$

Molecular models suggest that these values are reasonable.

Remarks. – 1. The linear combinations obtained with the matrix elements given in table 2 and in (11) are

$$
\begin{aligned}
\mathbf{3}: \quad & \psi_1 = 0.84\,\pi - 0.54\,n_O \\
& \psi_2 = 0.54\,\pi + 0.84\,n_O \\
\mathbf{6}: \quad & \psi_1 = 0.89\,n_S - 0.45\,\pi \\
& \psi_2 = 0.45\,n_S + 0.89\,\pi
\end{aligned}
\tag{13}
$$

In contrast the corresponding linear combinations ψ_1, ψ_2 of **4** and **7** are for all practical purposes, fifty-fifty mixtures of π and n_X (X = O, S).

A survey of available experimental data indicates that the full width at half height (FWHH) of a 'pure' π-, n_O- or n_S-PE. band has the value 0.55 eV, 0.45 eV or 0.20 eV respectively, with rather little variation from one compound to another. From (13) we would expect that in the PE. spectrum of **3** band ① ought to be wider than band ②, whereas the reverse should be true for the spectrum of **6**. Indeed we observe FWHH ① $= 0.65$ eV $>$ FWHH ② $= 0.35$ in **3**, but FWHH ① $= 0.25$ eV $<$ FWHH ② $= 0.40$ eV in **6**. For **4** and **7** both bands ① and ② should have the same FWHH. In the case of **7** the PE. spectrum yields FWHH ① $=$ FWHH② $= 0.40$ eV. (In the case of **4** band ② overlaps with the σ-band system at higher ionization energies, so that the prediction can not be checked.)

2. A check of the interaction matrix element $B_{\pi n_O} = -1.2$ eV deduced from the PE. spectrum of **4** is provided by the PE. spectroscopic data observed for unsubstituted 4,5-dihydropyrane (**12**) and vinylisopropylether (**13**).
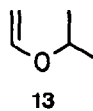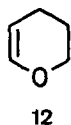

The ionization energies of the first two bands in the PE. spectrum of **12** are $I_{v,1} = 8.6_0$ eV and $I_{v,2} = 11.0_5$ eV, i.e. shifted by $\delta I_1 = 0.2$ and $\delta I_{v,2} = 0.2_5$ eV towards higher energies than the corresponding bands in the PE. spectrum of **4**. The fact that both bands are shifted equally is consistent with the assumption that the two orbitals are mainly fifty-fifty mixtures of π and n_O. The sum $\delta I_{v,1} + \delta I_{v,2} = 0.4_5$ eV is of the correct order of magnitude, but perhaps a bit on the low side of the expected value of 0.6 to 0.7 eV [32]. The split $I_{v,2} - I_{v,1} = 2.4_5$ eV is the same as the one observed for **4**, which confirms the value $B_{\pi n_O} = -1.2$ eV given in (11).

As shown in Tab. 2 the basis energies for **13** are $A'(\pi) = -10.1_5$ eV and $A'(n_O) = -9.7$ eV. From these values and from $I_{v,1} = 8.9$ eV, $I_{v,2} = 11.2$ eV we obtain $B_{\pi n_O} = -1.1_5$ eV to -1.2_5 eV, depending on the approximation, i.e. again in excellent agreement with the value given in (11).

3. From the analysis of the PE. spectra of **6** and **7**, in particular in comparison to their oxygen analogues **3** and **4**, it is obvious that the results can be perfectly rationalized without invoking the participation of sulfur d-orbitals.

Table 2. *Basis energies* $A'(\varphi)$, $A'(\phi)$ *for molecules* $M(\varphi,\phi)$. The values are calculated according to (6) with the shift parameters $\delta A_\phi(\varphi)$ given in (10). $\overline{A}' = (A'(\varphi) + A'(\phi))/2$; $\bar{\varepsilon} = (\varepsilon_1 + \varepsilon_2)/2$, ε_1 and ε_2 being 'observed' molecular orbital energies $\varepsilon_j = -I_{v,j}$. All values in eV

Upper part (sulfur compounds):

$A'(\pi)$ = - 9,6 ; ε_1 = - 8,5 [27]
$A'(n_S)$ = - 8,7 ; ε_2 = - 0,8$_5$
$\overline{A}'$ = - 9,1$_5$; $\bar{\varepsilon}$ = - 9,2

$A'(\pi)$ = - 9,4 ; ε_1 = - 8,6 [25]
$A'(n_S)$ = - 9,0$_5$; ε_2 = -10,0$_5$
$\overline{A}'$ = - 9,4$_5$; $\bar{\varepsilon}$ = - 9,3

$A'(\pi)$ = - 9,1 ; ε_1 = - 7,9$_5$
$A'(n_S)$ = - 8,7 ; ε_2 = - 9,9$_5$
$\overline{A}'$ = - 8,9 ; $\bar{\varepsilon}$ = - 8,9$_5$

$A'(\pi)$ = - 8,7 ; ε_1 = - 8,3$_5$
$A'(n_S)$ = - 8,4$_5$; ε_2 = - 8,8$_5$
$\overline{A}'$ = - 8,6 ; $\bar{\varepsilon}$ = - 8,6$_5$

$A(\pi)$ = - 9,2 [29]
$A(n_S)$ = - 8,4 [27, 28]

$A(n_O)$ = - 9,4 [25, 31]
$A(n_S)$ = - 8,4$_5$ [25]

$A(\pi)$ = - 8,7
$A(n_S)$ = - 8,4$_5$

$A(\pi)$ = - 8,3
$A(n_S)$ = - 8,2$_5$

Lower part (oxygen compounds):

$A'(\pi)$ = - 9,8$_5$; ε_1 = - 9,1$_5$ [24]
$A'(n_O)$ = - 9,8$_5$; ε_2 = -10,6
$\overline{A}'$ = - 9,8$_5$; $\bar{\varepsilon}$ = - 9,9

$A'(\pi)$ = -10,1$_5$; ε_1 = - 8,9 [30]
$A'(n_O)$ = - 9,7 ; ε_2 = -11,2
$\overline{A}'$ = - 9,8$_5$; $\bar{\varepsilon}$ = -10,0$_5$

$A'(\pi)$ = - 9,3$_5$; ε_1 = - 8,4
$A'(n_O)$ = - 9,7 ; ε_2 = -10,8
$\overline{A}'$ = - 9,5$_5$; $\bar{\varepsilon}$ = - 9,6

$A'(\pi)$ = - 9,0 ; ε_1 = - 8,6
$A'(n_O)$ = - 9,3$_5$; ε_2 = - 9,4$_5$
$\overline{A}'$ = - 9,1$_5$; $\bar{\varepsilon}$ = - 9,0$_5$

$A(\pi)$ = - 9,2 [29]
$A(n_O)$ = - 9,5$_5$ [24]

$A(\pi)$ = - 9,5 [17, 19]
$A(n_O)$ = - 9,4 [18, 23]

$A(\pi)$ = - 8,7
$A(n_O)$ = - 9,3$_5$

$A(\pi)$ = - 8,3$_5$
$A(n_O)$ = - 9,0$_5$

4. It has been recently pointed out that the highest occupied σ-orbitals in the six-membered ring of norbornane derivatives cannot interact with a p-orbital in position 7, due to the symmetry of these 'ribbon orbitals' [33] (diagrams (a) and (b)):

$$(12)$$

(a)AA   (b)SS   (c)SA
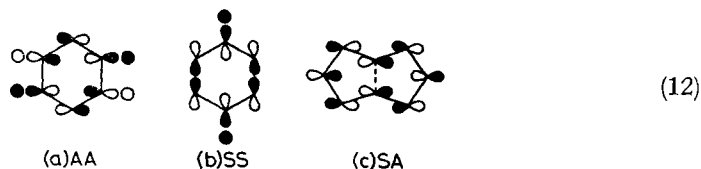
In molecules, such as 7-oxanorbornane [24] or 7-thianorbornane [28] this lack of interaction, and thus of the corresponding destabilization of the lone-pair orbitals n_O or n_S, leads to relatively high ionization energies for the first band in the PE. spectra of these compounds, as compared to similarly substituted, open chain ethers or sulfides. It is interesting that one of the ribbon-orbitals of 9-oxa- (2) and 9-thia-bicyclo[3.3.1]nonane (5) (see c) of (12)) has the proper symmetry to interact with a p-orbital in position 9 and that we should therefore expect relatively small values for the first ionization potentials of these molecules, if compared to their open-chain analogues. As has been mentioned above, this is indeed the case.

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55. p-Hydroxybenzylierung von Carbanionen mit Chinonmethid-liefernden Verbindungen[1])

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(28. XI. 75)

p-Hydroxybenzylation of Carbanions with Quinonemethide Precursors. – *Summary* 3,5-Dialkylated 4-hydroxy-benzyl derivatives **4, 5** and **6** are useful starting materials for th p-hydroxybenzylation of carbanions derived from activated methylene compounds **7**. The reactioi presumably proceeds through intermediate formation of quinonemethides **2**. The scope of th reaction is discussed.

Einleitung. – Sterisch gehinderte Phenole der Struktur **1** haben wegen ihre
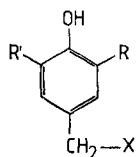
R, R' = (verzweigtes) Alkyl

1

Fähigkeit, autooxydative Radikalprozesse in Polymeren zu unterdrücken, grosse industrielle Bedeutung als Antioxydantien («Radikalfänger») [1].

Ist der Substituent X in **1** über ein Heteroatom an das Benzylkohlenstoffatom gebunden, so beobachtet man häufig beim Einsatz solcher Verbindungen zur Poly-

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[1])   Der systematische Name von Chinonmethid ist 4-Methyliden-cyclohexa-2,5-dienon.