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n-π INTERACTIONS IN HOMOALLYLIC METHYL ETHERS A PHOTOELECTRON SPECTROSCOPIC STUDY

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Abstract—The He I photoelectron spectra of several monocyclic and bicyclic methoxy compounds have been interpreted in terms of inductive effects and n-π interactions between the π_{CC} molecular orbital and the oxygen lone pair orbital n_o. The n-π interactions appear to be small, and are mainly through bond.

In recent years photoelectron spectroscopy has proved to be an excellent technique for the accurate determination of ionization potentials. Since electronic interactions have a marked influence on the values of ionization potentials, photoelectron spectroscopy offers a suitable experimental method for their investigation. Heilbronner *et al.*[1-4] have described interactions between π-electrons (π–π interactions) in conjugated and non-conjugated molecules. Also interactions between lone pair electrons and π-electrons (n-π interactions)[5-7] and between lone pair electrons (n–n interactions)[8-12] have been established in various cases.

In recent publications[13-20] dealing with monocyclic and bicyclic unsaturated ketones and ethers, the photoelectron spectra of these compounds have been interpreted by correlation with the spectra of the corresponding saturated compounds and alkenes. Differences between ionization potentials of a cyclic unsaturated ketone and the corresponding model compounds have been interpreted in terms of inductive effects and of interaction between the π_{CC} and the oxygen lone pair molecular orbital n_o.

Values of inductive shifts of molecular orbitals and interactions between the π_{CC} and the nitrogen lone pair molecular orbital n_N in several unsaturated bicyclic compounds have been derived by Schmidt *et al.*[21]†

In this publication results are presented for a series of monocyclic and bicyclic methoxy compounds. Inductive effects and n–π interactions in these molecules are estimated.

EXPERIMENTAL

The photoelectron spectra were recorded on a Vacuum Generators model ESCA 3 photoelectron spectrometer, equipped with a hemispherical analyser and using the He 584 Å line (excitation energy 21·21 eV). Calibration of the ionization energy scale was carried out using known ionization energy values of Ar as a standard. The resolution obtained in the present work was about 25 meV. The optimum instrument resolution is 12 meV (full width at half height of the Ar doublet).

RESULTS AND DISCUSSION

Photoelectron spectra of several monocyclic and bicyclic methoxy compounds (see Fig. 1) have been recorded. The vertical ionization potentials due to the π_{CC} and n_o band are given in Table 1. The ionization potentials of the π_{CC} band of the corresponding alkenes **13–16** are tabulated as well. The first photoelectron band of compounds **8–12** must be ascribed to ionization from the oxygen lone pair orbital n_o. In the molecules **13–16** the first band corresponds to π_{CC} ionization.[1,3] Band assignments in the spectra of compounds **1–7** were made by comparison with the spectra of the alkenes **13–16** and of the methyl ethers **8–12**. In 4-methoxy-cyclopentene **1** and 4-methoxycyclohexene **2** the first photoelectron band shows vibrational structure (1410 and 1490 cm^{-1} respectively, ±50 cm^{-1}), which indicates that this band must be ascribed to ionization of a bonding electron from the π_{CC} orbital. The second band is relatively sharp and must be due to the oxygen lone pair orbital n_o. In the other unsaturated methyl ethers **3–7** neither of the two bands shows a distinguishable vibrational structure. On account of the assignment in **1** and **2**, and by comparison with the ionization potentials in the corresponding molecules **10**, **11**, **12**, **15**, **16**, the first photoelectron band in compounds **3–7** is assigned to ionization from the π_{CC} orbital.

The n-π interaction and inductive shifts are described with the parameters given in Fig. 2. As in Ref 15, inductive shifts δA_π and δA_n of the molecular orbitals A_π^0 and A_n^0 in the model molecules **13** and **8** are assumed. The corrected levels are designated by A_π and A_n. The interaction $B_{\pi,n}$ between the π_{CC} orbital and the oxygen lone pair orbital n_o

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† In a recently published paper Schmidt *et al.*[21] conclude that there is no n-π interaction in 9-azabicyclo[4.2.1]non-7-ene and 9-azabicyclo[4.2.1]nona-2,4-diene, but claim that the situation is drastically different in 9-azabicyclo[4.2.1]nona-2,4,7-triene. In the latter molecule they obtain a conjugative interaction between the nitrogen lone pair orbital with two π_{CC} orbitals (0·35 and 0·45 eV). Interpreting their measurements according to Eqn (1), for 9-azabicyclo[4.2.1]non-7-ene a $B_{\pi,n}$ close to zero, for 9-azabicyclo[4.2.1]nona-2,4-diene a small $B_{\pi,n} \approx 0{\cdot}1$ eV, and for 9-azabicyclo[4.2.1]nona-2,4,7-triene two larger n-π interactions (0·4 and 0·5 eV) are obtained, resulting in a more gradual increase in $B_{\pi,n}$ along the series of molecules studied.

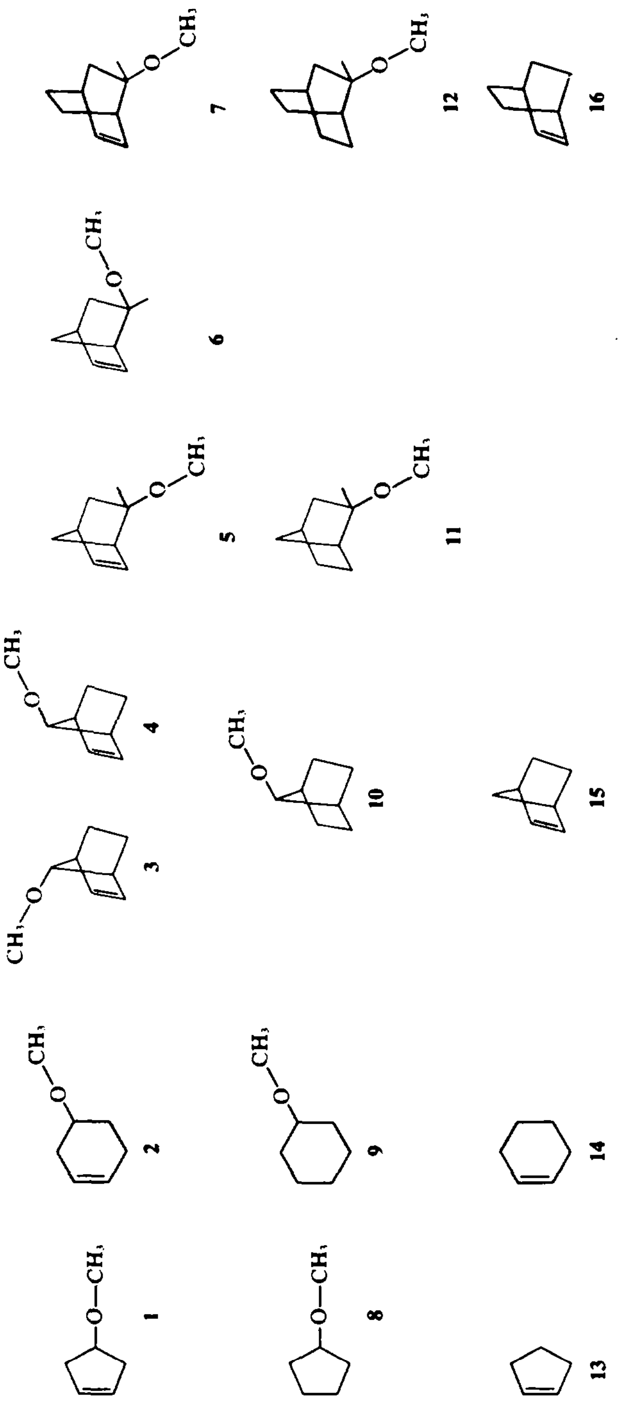

Fig. 1.

Table 1

Vertical ionization potentials (eV)[a]		(π)	(n)
4-methoxycyclopentene	**1**	9·12	9·57
4-methoxycyclohexene	**2**	9·01	9·40
syn-7-methoxybicyclo[2.2.1]hept-2-ene	**3**	8·84	9·40
anti-7-methoxybicyclo[2.2.1]hept-2-ene	**4**	9·02	9·52
endo-5-methoxybicyclo[2.2.1]hept-2-ene	**5**	8·69	9·37
exo-5-methoxybicyclo[2.2.1]hept-2-ene	**6**	8·68	9·51
endo-5-methoxybicyclo[2.2.2]oct-2-ene	**7**	8·77	9·27
methoxycyclopentane	**8**		9·40
methoxycyclohexane	**9**		9·22
7-methoxybicyclo[2.2.1]heptane	**10**		9·27
endo-5-methoxybicyclo[2.2.1]heptane	**11**		9·17
endo-5-methoxybicyclo[2.2.2]octane	**12**		9·07
cyclopentene[3]	**13**	9·18	
cyclohexene[1]	**14**	9·12	
bicyclo[2.2.1]heptene[1]	**15**	8·97	
bicyclo[2.2.2]octene[1]	**16**	9·05	

[a] ±0·03 eV.

Table 2. n-π Interaction and inductive shifts (in eV) for $\delta A_\pi/\delta A_n = 1$

		$B_{\pi,n}$	$\delta A_\pi = \delta A_n$
4-methoxycyclopentene	**1**	$0{\cdot}1_2$	$0{\cdot}0_6$
4-methoxyclohexene	**2**	$0{\cdot}1_4$	$0{\cdot}0_4$
syn-7-methoxybicyclo[2.2.1]hept-2-ene	**3**	$0{\cdot}1_3$	$0{\cdot}0_0$
anti-7-methoxybicyclo[2.2.1]hept-2-ene	**4**	$0{\cdot}1_0$	$0{\cdot}1_5$
endo-5-methoxybicyclo[2.2.1]hept-2-ene	**5**	$0{\cdot}2_4$	$-0{\cdot}0_4$
exo-5-methoxybicyclo[2.2.1]hept-2-ene	**6**	$0{\cdot}3_1$	$0{\cdot}0_2$
endo-5-methoxybicyclo[2.2.2]oct-2-ene	**7**	$0{\cdot}2_4$	$-0{\cdot}0_4$

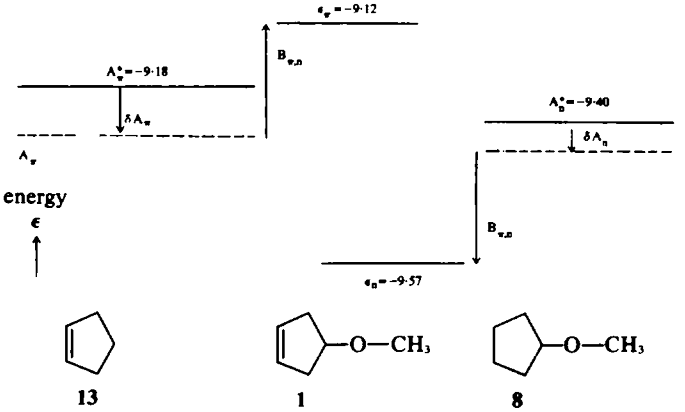

Fig. 2. Correlation diagram of the highest occupied M.O.'s of **13**, **1** and **8**. The negative values of the vertical ionization potentials are assumed to be equal to the orbital energies.[22]

in **1** manifests itself in a stabilization of A_n and a destabilization of A_π. For interactions involving the n_o and π_{CC} levels, the following equations are obtained:[15]

$$\epsilon_\pi = A_\pi^0 - \delta A_\pi + B_{\pi,n}$$
$$\epsilon_n = A_n^0 - \delta A_n - B_{\pi,n}. \tag{1}$$

In these equations ϵ_π and ϵ_n are the negative values of the first and second ionization potentials of molecules **1**–**7**. A_π^0 and A_n^0 have a similar meaning for molecules **8**–**16**. The interaction $B_{\pi,n}$ between the π_{CC} orbital and the oxygen lone pair n_o is determined by making an assumption for the ratio $\delta A_\pi/\delta A_n$ for the entire series of molecules measured. Values of $B_{\pi,n}$, obtained with $\delta A_\pi/\delta A_n = 1$ and $\delta A_\pi/\delta A_n = 4$ (compare Ref 15), are given in Tables 2 and 3.

The inductive effects appear to be small (<0·1 eV), with the exception of *anti*-7-methoxybicyclo[2.2.1]hept-2-ene **4**, for which deviating values have been obtained. These deviations and the occasional small negative values for δA_π and δA_n give an indication of the limitations of this approach.

For all molecules measured, the interaction $B_{\pi,n}$ between the π_{CC} orbital and the oxygen lone pair orbital n_o is small: $B_{\pi,n} \leq 0{\cdot}3$ eV. $B_{\pi,n}$ is influenced by the value of the ratio $\delta A_\pi/\delta A_n$ only to a small extent, and therefore the trend of the $B_{\pi,n}$ values along the series of molecules remains approximately the same. However, the value of $B_{\pi,n}$ for *anti*-7-methoxybicyclo[2.2.1]hept-2-ene is clearly dependent on the particular value of the ratio $\delta A_\pi/\delta A_n$ adopted.

The interaction between the C=C double bond and the oxygen lone pair can occur both directly through space, and through bond.[23] If the through space interaction would be the dominating factor, the value of the interaction parameter $B_{\pi,n}$ should be influenced by the position of the methoxy group with regard to the double bond. However, the relatively small differences between the $B_{\pi,n}$'s, observed throughout our series of unsaturated compounds, indicate that through space interaction is of minor importance and that through bond interaction

Table 3. n-π Interaction and inductive shifts (in eV) for $\delta A_\pi / \delta A_n = 4$

		$B_{\pi,n}$	δA_π	δA_n
4-methoxycyclopentene	**1**	$0{\cdot}1_4$	$0{\cdot}0_8$	$0{\cdot}0_2$
4-methoxycyclohexene	**2**	$0{\cdot}1_6$	$0{\cdot}0_4$	$0{\cdot}0_1$
syn-7-methoxybicyclo[2.2.1]hept-2-ene	**3**	$0{\cdot}1_3$	$0{\cdot}0_0$	$0{\cdot}0_0$
anti-7-methoxybicyclo[2.2.1]hept-2-ene	**4**	$0{\cdot}1_9$	$0{\cdot}2_4$	$0{\cdot}0_6$
endo-5-methoxybicyclo[2.2.1]hept-2-ene	**5**	$0{\cdot}2_1$	$-0{\cdot}0_8$	$-0{\cdot}0_2$
exo-5-methoxybicyclo[2.2.1]hept-2-ene	**6**	$0{\cdot}3_3$	$0{\cdot}0_4$	$0{\cdot}0_1$
endo-5-methoxybicyclo[2.2.2]oct-2-ene	**7**	$0{\cdot}2_1$	$-0{\cdot}0_8$	$-0{\cdot}0_2$

prevails. Another indication for the importance of through bond interaction is that $B_{\pi,n}$ in **5**, **6** and **7** is considerably larger than in **1**, **2** and **3**, in spite of a geometrically less favourable position of the methoxy group for through space interaction. Our conclusion that the interaction is mainly through bond is supported by recent photoelectron spectroscopic results of Schmidt *et al.*[16,18] on 2,5-dihydrofuran and 2,5-dihydrothiophen. Also, there is chemical evidence for through bond interactions in transition states of ionizations of *endo*-2-tosyloxy-7-alkoxynorbornanes[24] and in *endo*-additions to 7-substituted norbornenes.[25]

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