

UPS Study of [2,2](2,5)Furanophane and [2,2](2,5)Thiophenophane Evidence Regarding the Importance of Through Bond and Through Space Interactions

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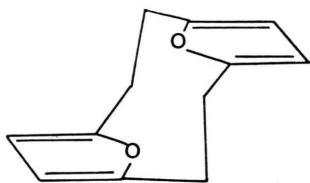
The ultraviolet photoelectron spectra of [2,2](2,5)furanophane (FUPH) and [2,2](2,5)thiophenophane (THPH) have been analyzed on the basis of a perturbational molecular orbital analysis, by comparison with CNDO/2 computations and by correlating them with the spectra of related molecules. Through space and through bond interactions between the two hetero-aromatic rings are shown to be important in determining the ordering of the outermost MO's in this class of compounds.

Introduction

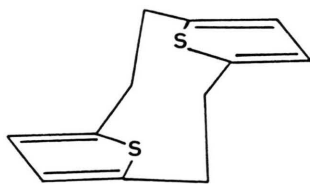
A large number of investigations has been carried out [1] on [2,2]metacyclophanes and a number of [2,2]phanes with other aromatic nuclei, whose molecular architecture raises many interesting theoretical questions with regard to the importance of through bond and through space interactions [2].

through bond interactions are operating. The most peculiar and interesting through space interactions are those between the nitrogen lone pairs and the π system of the two pyridine rings.

The recent availability of the X-ray structure [8] of the homologues [2,2](2,5)furanophane (FUPH) and [2,2](2,5)thiophenophane (THPH) * prompted

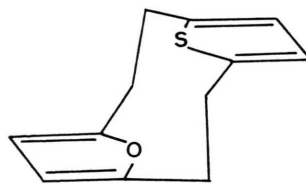


FUPH



THPH

scheme 1



FUTHPH

In spite of the fact that ultraviolet photoelectron spectroscopy (UPS) is a powerful tool for investigating such types of interactions [3, 4], very few attempts [5, 6] have been made with the technique to analyse the electronic structure of this class of compounds. In particular we have recently reported [7] the UPS spectrum of [2,2](2,6)pyridinophane (PYPH). In this molecule, both through space and

through bond interactions are operating. The most peculiar and interesting through space interactions are those between the nitrogen lone pairs and the π system of the two pyridine rings.

* The molecules of both compounds are centrosymmetric and approximate well to C_{2h} symmetry. The heteroatoms are displaced away from the aromatic rings (S, 0.196 Å; O, 0.082 Å) which are parallel and separated by 2.63 and 2.34 Å in THPH and FUPH, respectively. The sulphur-sulphur and oxygen-oxygen distances are shorter than the expected van der Waal distances. Each oxygen atom makes short contacts also with the two ortho carbon atoms of the opposite ring, whereas each sulphur atom makes short contacts with all the carbon atoms of the opposite ring and lies nearly above its middle point [8].

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spectra of 2,5-dimethylfuran and 2,5-dimethylthiophen has been included to assist in the interpretation of the spectra of the phanes, given that the latter systems can be considered to be formed by welding together two of the mononuclear compounds.

Experimental

The UPS spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer. The He I resonance line at 584 Å (21.22 eV) served as the ionization source. The spectra were calibrated against Ar and Xe lines. The accuracy of the ionization energy (IE) values is estimated to be ± 0.05 or ± 0.1 eV depending upon the number of decimals quoted in the Tables.

FUPH and THPH were obtained from 5-methyl-2-furfuryl and 5-methyl-2-thienyl-trimethylammonium hydroxide respectively, according to the procedure proposed by Wynberg *et al.* [9]. FUTHPH was obtained, in a mixture with compounds FUPH and THPH, as described [10]. The separation of the compounds was achieved by gaschromatography (5% weas on chromosorb W 30–60 mesh, column temp. 170 °C, helium as carrier gas). Final crystallization from petroleum ether led to a product having m.p. 198–199° (found: C 70.6; H 5.9; S 15.6. C₁₂H₁₂OS requires: C 70.5; H 5.9; S 15.7%). 2,5-dimethylfuran and 2,5-dimethylthiophen were commercial products purified by fractional vacuum distillation.

Results and Discussion

The low IE region of the spectra of FUPH and THPH are shown in Fig. 1, while the IE values of the various bands below 10 eV are listed in Table 1. At higher IE's the bands are not well resolved and they will not be analysed here.

Table 1. Ionization energy values (eV) from the UPS spectra of [2,2](2,5)furanophane (FUPH), [2,2](2,5)thiophenophane (THPH) and [2,2](2,5)furanothiophenophane (FUTHPH). See the text for the assignment of the ionization energy values to the corresponding MO's.

	I_1	I_2	I_3	I_4
FUPH	7.50	8.14	9.6	9.6
THPH	7.9	7.9	8.2	9.08
FUTHPH	7.83	8.06	8.67	9.71

The assignment of both spectra is based on a Perturbational Molecular Orbital (PMO) analysis [2]. In addition we have carried out CNDO/2 calculations [11] at the experimentally determined geometries [8]. The PMO analysis presented here focusses upon the orbital interactions occurring between the two identical fragments obtained from

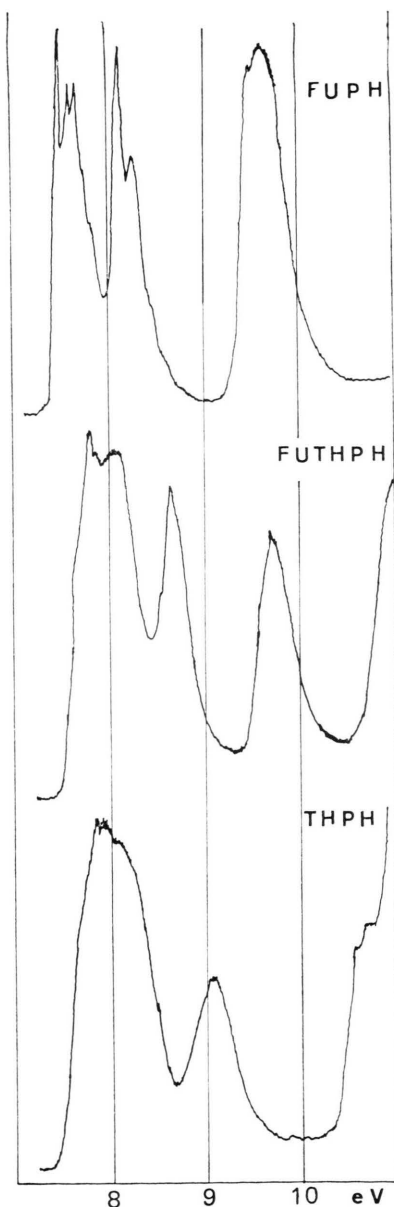


Fig. 1. Low ionization energy region of the UPS spectra of [2,2](2,5)furanophane (FUPH), [2,2](2,5)thiophenophane (THPH) and [2,2](2,5)furanothiophenophane (FUTHPH).

Table 2. Ionization energy values (eV) from the UPS spectra of furan, thiophen and their 2-methyl and 2,5-dimethyl derivatives.

	π_3	π_2	First σ or π_1
2,5-dimethylfuran	7.90	9.73	12.3
2-methylfuran	8.37	10.00	12.6
furan ^a	8.89	10.32	14.4
2,5-dimethylthiophen	8.02	9.00	11.6
2-methylthiophen ^b	8.43	9.23	11.75
thiophen ^c	8.87	9.49	12.1

^a From References [3] and [13]. ^b From References [12].^c From References [3] and [14].

FUPH and THPH respectively by breaking the two central C—C bonds of the bridges. The ordering and type of the first MO's of these two basic fragments are taken to be the same as in 2,5-dimethylfuran and 2,5-dimethylthiophen, respectively. In the latter compounds the first two bands can easily be assigned, on the basis of the assignments of the spectra of the corresponding 2-methyl derivatives [12] and of the spectra of furan [3, 13] and thiophen [3, 14], respectively, to π_3 , the antisymmetric MO of furan and thiophen, and to π_2 , the symmetric MO of furan and thiophen. On the same basis the third band will probably correspond to ionization from a σ MO. The corresponding IE values are listed in Table 2. From the comparison of these values, it is of interest to point out that the effect of two methyl groups upon the energies of π_3 and π_2 is nearly additive [15] and slightly larger for furan than thiophen. The effect on π_3 is of the same order of magnitude as that reported for the highest occupied molecular orbital (HOMO) of benzene (~ 0.5 eV) [16].

We proceed now to discuss the spectrum of FUPH, which shows three bands below 10 eV; the intensity of the third band suggests that two ionization events occur at nearly the same energy. Our discussion is based upon the interactions occurring between the two identical fragments obtained from FUPH, and in particular upon the interactions of π_3 and π_2 of one fragment with the corresponding MO's of the other fragment. The interactions are considered to occur in steps, the first being between MO's of the same energy. Therefore the interaction between the two π_3 and the two π_2 will give rise to the corresponding in

phase (π_3^+ and π_2^+) and out of phase (π_3^- and π_2^-) combinations. (The π_3^+/π_3^- splitting will not be large at this stage since the two π_3 MO's do not overlap appreciably because the electron density at the oxygen atoms is zero.) These MO's can now interact mainly with inner MO's of suitable symmetry. From our previous experience with PYPH [7] we expect the most important interactions to be those with the in phase ($\sigma_{CC_v}^+$) and out of phase ($\sigma_{CC_v}^-$) combinations of the two σ_{CC_v} bonds localized in the two bridges. In particular, π_3^+ (A_u in C_{2h} symmetry [8]) can interact with $\sigma_{CC_v}^-(A_u)$, and $\pi_2^+(A_g)$ with $\sigma_{CC_v}^+(A_g)$, while $\pi_2^-(B_u)$ and $\pi_3^-(B_g)$ can not interact with $\sigma_{CC_v}^+$ and/or $\sigma_{CC_v}^-$ for symmetry reasons.

Furthermore, because of the different magnitudes [17] of the coefficients of C_2 and C_5 in π_3 and π_2 , the interaction $\pi_3^+/\sigma_{CC_v}^-$ is expected to be significant, while $\pi_2^+/\sigma_{CC_v}^+$ is expected to be small.

In addition, other high-lying σ MO's with non-zero contributions from the p_z and/or p_x atomic orbital of the heteroatom such as $\sigma_{O_z}^+(A_g)$ and $\sigma_{O_z}^-(B_g)$ (these and other relevant group orbitals are sketched in Fig. 2) will be expected to mix with appropriate combinations of the outer π MO's, as found for the pyridine lone pair combinations in PYPH [7]. In the present case, however, these interactions will be sizeably smaller because of the absence of a "lone pair" highly localized at the oxygen atom and because of the different energy gap between the interacting MO's.

The CNDO/2 results are in good agreement with this reasoning. The HOMO (-10.14 eV), in fact, is found to be mainly π_3^+ with a certain admixture of $\sigma_{CC_v}^-$, while the next HOMO (-11.43 eV) is found to be mainly π_3^- with a small admixture of $\sigma_{O_z}^-$. The parentages suggest in fact that in the HOMO the contribution of the π MO's is about 75% and that of the $\sigma_{CC_v}^-$ MO about 13%, while in the next HOMO the contribution of the π MO's is about 85% and that of the $\sigma_{O_z}^-$ about 8%. Consequently, the interaction between π_3^+ and $\sigma_{CC_v}^-$ is such to raise π_3^+ , which prior to this interaction was at slightly lower energy than π_3^- , above it.

According to the CNDO/2 results, the next MO (-14.40 eV) is a σ MO (mainly $\sigma_{O_z}^-$ and $\sigma_{C-C_z}^-$), followed by an almost degenerate pair of π MO's at -14.52 and -14.57 eV (mainly π_2^+ and π_2^- respectively). The ionization energy values of the parent compounds listed in Table 2 clearly indicate

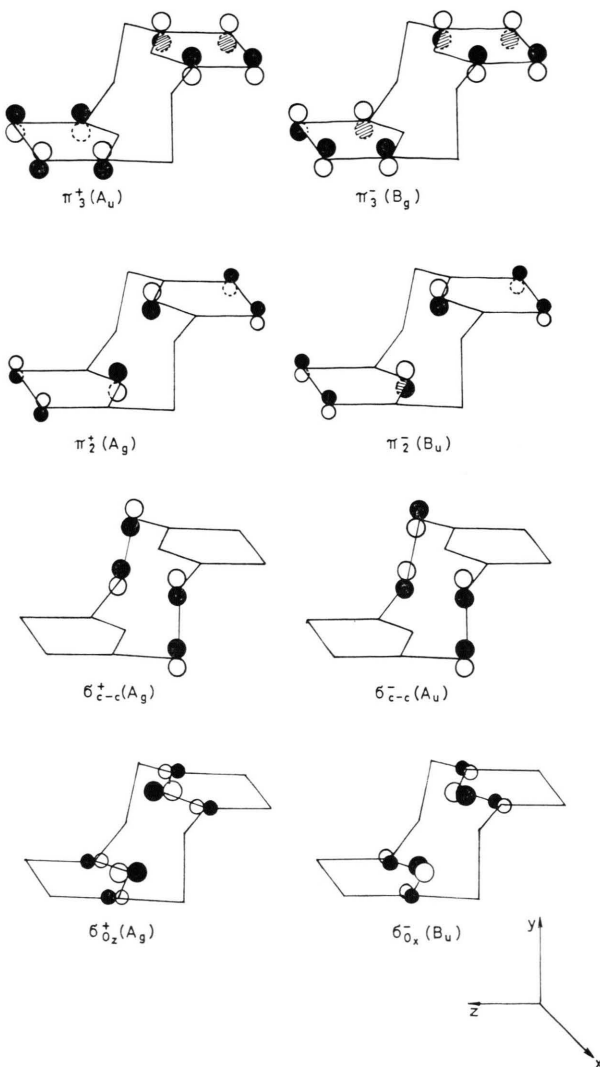


Fig. 2. Sketches of the relevant group orbitals contributing to the outermost MO's of [2,2]-metacyclophanes. Only the most important atomic contributions are shown.

that the presence of a σ MO between the two pairs of π MO's is an artifact of this kind of computation. CNDO/2 results are, in fact, usually trustworthy when the comparison is limited to MO's of similar symmetry. This situation shows also the advantage of associating the CNDO/2 results with a PMO analysis that provides a certain logical guide to the computational results. The near degeneracy between π_2^+ and π_2^- is a consequence of the smaller interaction of π_2^+ with $\sigma_{CC_v}^+$ and $\sigma_{O_x}^+$ that raises the energy of π_2^+ less than in the case of π_3^+ .

Actually, according to the CNDO/2 calculations, π_2^+ is positioned 0.05 eV above π_2^- . This energy order for the four outermost MO's, (i.e. $\pi_3^+ > \pi_3^- > \pi_2^+ > \pi_2^-$) seems therefore plausible on the basis of our previous PMO reasoning and provides a satisfactory interpretation of the experimental results.

The UPS spectrum of THPH shows a broad intense band peaking at 7.9 eV with a shoulder at 8.2 eV, and a second band at 9.08 eV (see Figure 1). The fact that the area of the latter band is about one third of that of the first composite band is an indication that three ionization events contribute to the first band and only one to the second.

The interpretation of the spectrum is done on the basis of a PMO analysis similar to that described before. In particular, on energy grounds, the mixings between the ring π MO's and σ_{CC} MO's are expected to be similar to those observed in FUPH, while, for the same reason, the mixings of π_3^- and π_2^+ with $\sigma_{S_x}^+$ and $\sigma_{S_z}^+$ respectively, are expected to be larger than in FUPH.

The computed results are in agreement with this reasoning and provide the following energy order:

$$\begin{aligned} & \pi_3^+ (-10.78 \text{ eV}) \\ & \cong \pi_3^- (-10.83 \text{ eV}) > \pi_2^+ (-11.32 \text{ eV}) \\ & > \pi_2^- (-11.46 \text{ eV}). \end{aligned}$$

According to the CNDO/2 results, the $\pi_2^+/\sigma_{S_z}^+$ and $\pi_3^-/\sigma_{S_x}^-$ interactions are, as expected, larger, the former because of a larger overlap (compare $S_{3p_z} - S'_{3p_z} = 0.0303$ with $O_{2p_z} - O'_{2p_z} = 0.0007$) that is mainly a consequence of the different geometry, and the latter because of a smaller energy gap in the sulphur species.

In Fig. 1 is shown also the spectrum of FUTHPH: it is evident that in the region below 10 eV the UPS spectrum of this compound is intermediate between those of FUPH and THPH. For FUTHPH the molecular structure can not be determined by X-ray analysis because of the random distribution of the sulphur and oxygen atoms in the crystal lattice [18]. (NMR results, however, indicate that its structure is more similar to that of THPH than that of FUPH [9, 10, 19].)

Consequently we have not carried out computations in this case, and the interpretation of the spectrum has been done solely in analogy with the spectra of FUPH and THPH. Accordingly, the energy order is expected to be also in this case: $\pi_3^+ > \pi_3^- > \pi_2^+ > \pi_2^-$.

Conclusions

The present study shows that: i) both through bond (e.g. π_3^+/σ_{CC}^- and π_2^+/σ_{CC}^+) and through space (e.g. π_3/π_3 , π_2/π_2), interactions are important in determining the ordering of the outermost MO's

in this class of compounds; and ii) the through space interaction between the ring π orbitals and the σ orbitals localized on the heteroatoms decreases in the order PYPH > THPH > FUPH.

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