

ELECTRONIC STRUCTURE AND REACTIVITY OF PROPELLANES

PHOTOELECTRON SPECTRA OF THIA[4.4.3]PROPELLANES

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Abstract—The photoelectron spectra of 12-thia[4.4.3]propell-3-ene (1), 12-thia[4.4.3]propell-3-ene-12-oxide (2), 12-thia[4.4.3]propella-3,8-diene-12-oxide (3), 12-thia[4.4.3]propella-3,8-diene-12-dioxide (4), 12-thia[4.4.3]propella-2,4-diene-12-oxide (5), 12-thia[4.4.3]propella-2,4,7,9-tetraene-12-oxide (6) and 12-thia[4.4.3]propella-2,4,7,9-tetraene-12-dioxide (7) have been investigated and the first bands have been interpreted. For compounds 3 and 4 the *endo-endo* conformation could be excluded. For 6 and 7 the interaction of the two butadiene moieties is of the same order as that of the π -orbitals in norbornadiene. The electronic structure of 3 and 4 allows us to rationalize and to predict the direction of the addition of cations and carbenes.

Polyenic propellanes are used as suitable models in the study of the stereochemistry of cycloaddition reactions and the interaction of semilocalized π -orbitals.¹⁻³ In connection with model calculations concerning the cycloaddition reactions of N-methyl and N-phenyl-triazoline-2,5-dione to the propellanes 6 and 7 we have studied the He(I) photoelectron (PE) spectra of these and related compounds. This investigation has been undertaken to obtain the sequence and energy of the highest occupied molecular orbitals (MO's) of the propellanes. This information is essential in the discussion of the reactivity of these compounds.

Here we report on the He(I) photoelectron (PE) spectra of 12-thia[4.4.3]propell-3-ene (1), 12-thia[4.4.3]propell-3-ene-12-oxide (2), 12-thia[4.4.3]propella-3,8-diene-12-oxide (3), 12-thia[4.4.3]propella-3,8-diene-12-dioxide (4), 12-thia[4.4.3]propella-2,4-diene-12-oxide (5), 12-thia[4.4.3]propella-2,4,7,9-tetraene-12-oxide (6) and 12-thia[4.4.3]propella-2,4,7,9-tetraene-12-dioxide (7).

Interpretation of the PE spectra

The first ionization potentials of 1 to 7 are collected in Table 1. To interpret these data we compare them with the PE spectra of related compounds. This procedure is adequate since the interaction of the SO or SO₂ moiety with the remainder is relatively small as far as the highest occupied MO's are concerned. Our interpretation is based on the assumption of the validity of Koopmans' theorem ($-\epsilon_j = I_{v,j}$).⁴ This theorem allows us to compare the measured vertical ionization potentials, $I_{v,j}$, with the calculated orbital energies, ϵ_j .

Structure of 4.4.3-propellanes. To calculate the orbital energies we use current semiempirical models: the Extended Hückel (EH)⁵, CNDO/2⁶ and in case of 1 the MINDO/3⁷ method. For these calculations the geometry of 1 and 7 in the gas phase is required. So far X-ray crystallographic investigations are available for two related propellanes, 11,13-dioxo-12-methyl-12aza[4.4.3]propella-3,8-diene (8)⁸ and 11,12-dioxo[4.4.2]propella-3,8-diene (9).⁹ In both cases the *exo-exo* conformation has been found in the solid state. This pref-

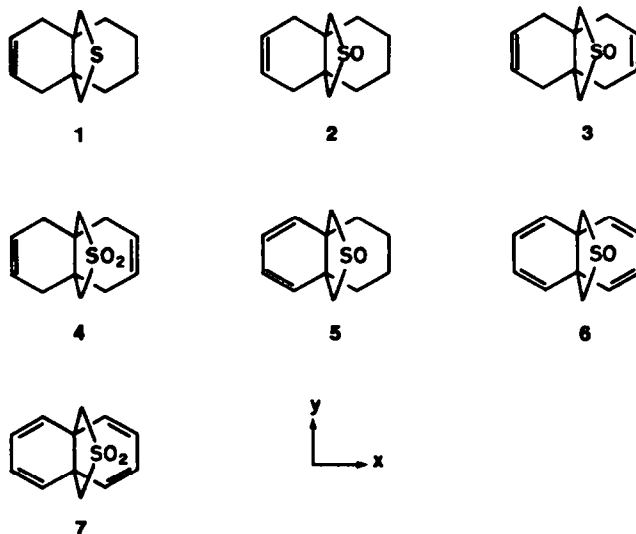
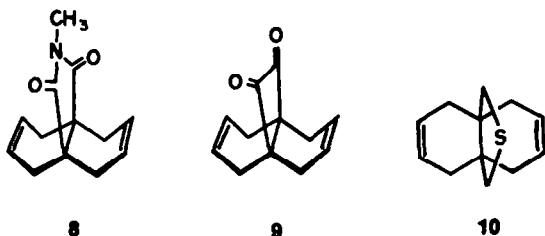


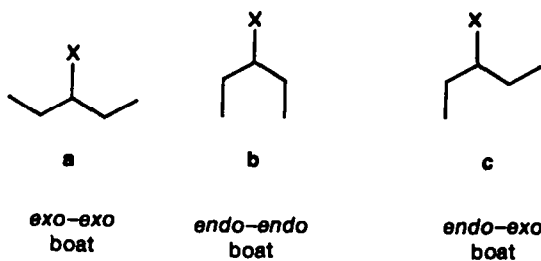
Table 1. Vertical ionization potentials $I_{V,j}$ (in eV) for the compounds 1 to 7 (All values in eV)

band	①		②		③		④		
	Compound	$I_{V,1}$	assignment	$I_{V,2}$	assignment	$I_{V,3}$	assignment	$I_{V,4}$	assignment
	1	8.07	a'(n)	9.06	a'(π)				
	2	8.50	a'(n)	9.35	a'(π)	9.5	a''(π _{SO})		
	3	8.52	a'(n)	9.1	a'(π ₊)	9.5	a'(π _{SO})	9.70	a'(π ₊)
	4	9.2	b ₁ (π ₋)	9.75	a ₁ (π ₊)	10.0	b ₁ (π _{SO})	10.7	a ₁ (σ _{SO})
	5	8.71	a''(π)	10.06	a''(π _{SO})	10.64	a'(σ _{SO})		
	6	8.44	a'(n)	8.56	a''(π)	8.9	a''(π)	9.9	a''(π _{SO})
	7	8.7	a ₂ (π)	8.9	b ₂ (π)	10.5	b ₁ (π _{SO₂})	11.0	a ₁ (σ _{SO₂})

erence of the *exo-exo* conformation can be explained as due to a secondary orbital interaction between the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) of 8 and 9 respectively.¹¹



Dreiding models suggest that in propelladienes similar to 8 or 9 (e.g. 3 or 4) the 6-membered rings should prefer the boat conformation. Besides the *exo-exo* boat conformation (a) encountered in 8 and 9 two other conformations, the *endo-endo* boat (b) and *endo-exo* boat (c) conformations seem quite likely. NMR studies on solutions of 3 and 4 reveal an equilibrium between the conformations b and c.¹²



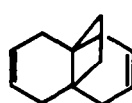
Our CNDO/2 calculations on 3 and 10 are in agreement with these results in so far as they predict only small energy differences between the conformations a, b and c as shown in Table 2.

PE Spectra of 1 to 4. In the PE spectrum of 1 we encounter two bands below 10 eV (① at 8.07 eV and ② at 9.06 eV) clearly separated by about 1 eV. The first band we ascribe to an ionization process from the sulfur 3p orbital, the second band is due to the ionization out of the π-orbital of the ethylene fragment. Our assignment of the first band is consistent with investigations on several thioethers¹³ with a similar number of carbons (pentamethylenesulfid shows a first IP at 8.45 eV). The

Table 2. Relative energies according to a CNDO/2 calculation of the conformations a, b and c of 3 and 10. The values are given in kcal/mol.

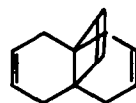
	conformation	energy
3a		0.31
3b		0.08
3b'		0.0
3c'		1.28
10a		0.23
10b		0.0
10c		0.92

ionization potentials recorded for 11 and 12^{3,14} are similar to the second ionization potential of 1.



11

IP₁ = 9.00 eV
IP₂ = 9.30 eV



12

IP₁ = 8.7 eV
IP₂ = 8.9 eV
IP₃ = 9.15 eV

This comparison corroborates our assignment of this band to the ionization process from the π -orbital of 1. All three semiempirical methods used to calculate the orbital energies support our assignment. The predicted energy difference $\epsilon(n) - \epsilon(\pi)$ for 1 is: 0.35 eV according to EH, 1.41 according to CNDO/2 and 0.30 according to MINDO/3.

The relatively low ionization potential for the 3p lone pair is due to a spatial interaction between the 3p lone pair and the π -orbital as indicated in Fig. 1.

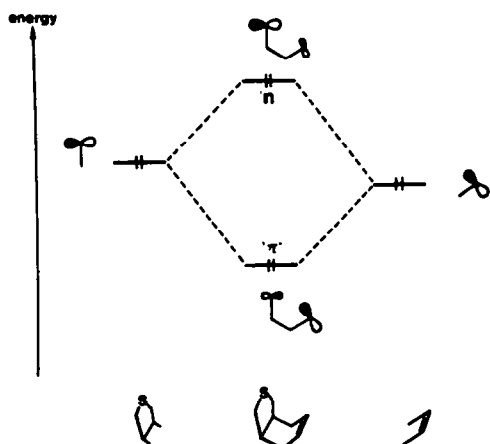
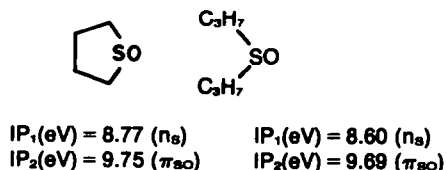
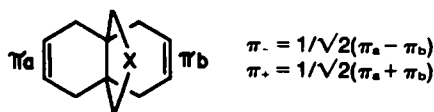


Fig. 1. Qualitative interaction diagram between the 3p lone pair on sulfur and the π -orbital in 1.

The PE spectrum of 2 exhibits two peaks below 10 eV. The ratio of the areas below the two peaks leads us to assign the first peak to one ionization process and the second one to two. In analogy with 1 we assign the first peak to ionization from the lone pair on the S atom. The second peak is due to ionization out of two π -orbitals localized mainly in the C-C double bond and in the SO bond, respectively. This assignment is supported by recent investigations of alkylsulfoxides¹⁵ as shown



below. Both examples show ionization potentials which are similar to those of 2. A clear determination of the sequence of the second and third band, π , π_{SO} or *vice-versa*, is not possible due to the strong overlap of these bands. EH calculations favour the assignment given in Table 1, CNDO/2 predict π_{SO} on top of π -olefin. The main difference between propellane 2 and propellane 3 is the presence of an additional π bond. According to experience^{3,16} with PE spectra of olefins the introduction of an additional π bond will lower the center of gravity of the basis orbital energies by about 0.15 eV. From experience with other propellanes³ and related molecules¹⁷ we expect for the *exo-exo* conformation of 3 a split of about 0.3 to 0.6 eV between the two linear combinations π_+ and π_- , as defined below (see also 11 and 12). With this estimate we assign bands ② and ③ as



due to the ionization out of π_- and π_+ orbitals respectively. The assignment of bands ① and ③ is straightforward. The values are very close to those recorded for n_s and π_{SO} in 2 (Fig. 2). A further confirmation of this assignment is given by comparison of the PE spectrum of 3 with 4. In the latter case we expect the lone pair on the sulfur center to disappear while the split between π_- and π_+ should remain constant. This is exactly what is observed (Fig. 2). The results of semiempirical calculations of the CNDO/2 and EH type on 3 and 4 adopting the *exo-exo*-, *endo-exo* and *endo-endo* conformation, are in agreement with these arguments. In the *endo-endo* conformation both methods predict for 3 a similar orbital energy for π_- and the sulfur lone pair, due to considerable through space interaction of the two π -orbitals, but this is not observed. The orbital energies predicted for the *exo-exo* and *endo-exo* conformations are very similar. PE spectroscopy is notable to differentiate between the two conformations.

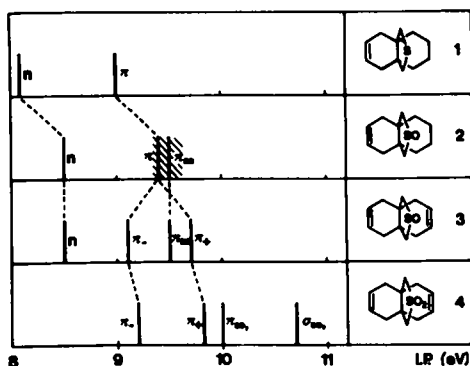
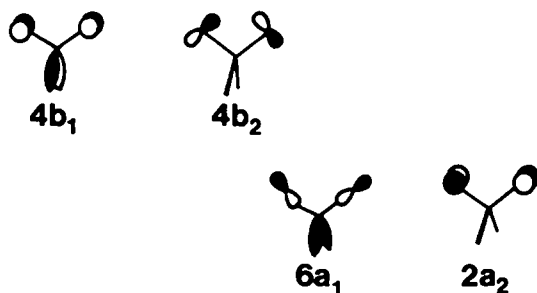


Fig. 2. Correlation of the first bands of the PE spectra of 1 to 4.

We assign bands ③ and ④ of 4 to orbitals mainly localized on the sulfone group. For the simplest known sulfone, dimethyl sulfone, the first four bands, corresponding to the highest occupied MO's, were assigned to $4b_1$, $4b_2$, $6a_1$ and $2a_2$.¹⁸ These four orbitals are shown below. The MO's $4b_1$ and $2a_2$ are of π -type, $4b_2$ is the



antisymmetric linear combination of the oxygen 2p orbitals and $6a_1$ can be considered as an S-O σ -orbital. According to an EH calculation the a_1 orbital is predicted to be above b_2 . This is due to a strong interaction of a_1

with the σ -frame. The assignment of bands ③ and ④ is thus b_1 and a_1 , as given in Table 1.

PE spectra of 5, 6 and 7. Common to 5, 6 and 7 is at least one butadiene π -fragment. A comparison with the PE spectrum of [4.4.2]propella-2,4,11-triene (13)³ leads us to expect the ionization potential corresponding to $a''(\pi)$ of the butadiene part of 5 between 8 and 9 eV. In accord with these expectations we assign the first band in the PE spectrum of 5 at 8.74 eV to $a''(\pi)$. In 6 and 7 there are two butadiene units present. Our reference



compound will be 14. From the comparison 13 to 14 we expect for 6 and 7 compared with 5 a split between $\epsilon(a_2)$ and $\epsilon(b_2)$ of about 0.4 eV and a slight increase in the center of gravity. This leads us to assign the second and third band of 6 (see also Fig. 3) and the first and second band of 7 as due to ionization events from $a_2(\pi)$ and $b_2(\pi)$. The measured split of 0.2 to 0.4 eV corresponds to



a resonance integral between the homoconjugating 2p atomic orbital of $\beta = -0.2$ to -0.4 eV. This agrees with values derived for 14 ($\beta = -0.4$ eV)³, bicyclo[2.2.2]octadiene ($\beta = -0.3$ eV) and *cis-cis-cis*-1,4,7-cyclononatriene ($\beta = -0.6$ eV).¹⁹ In the PE spectrum of 6 the first three bands are strongly overlapping, therefore the values given in Table 1 are affected by an error of *ca.* ± 0.1 eV. We assign the first band in the PE spectrum of 6 to an ionization process in which the electron vacates the sulfur lone pair since the corresponding band in the PE spectrum of 3 has a very similar value.

In analogy to 2 and 3 the fourth band in 6 is assigned to the ionization out of a π_{SO} orbital. A comparison between the PE spectra of 5 and 7 with the spectrum of 4 suggests assignment of the second and third band of 5 and the third and fourth band of 7 to ionization events from $b_1(\pi_{SO})$ and $a_1(\sigma_{SO})$ orbitals, respectively.

Concluding remarks

The analysis of the PE spectra of the propellanes 1 to 4 reveals two important corollaries concerning their structure and reactivity.

(1) For the propella-3,8-dienes 3 and 4 our results are only compatible with either an *exo-exo* boat conformation or an *exo-endo* boat conformation in the gas phase. This finding is supported by semiempirical calculations (Table 2).

(2) The orbital sequence derived for 1 allows us to rationalize and predict the direction of electrophilic additions to the double bond in 1 and related species like 13. To put forward our arguments we consider the MO which is mainly π in character. This is the second highest occupied orbital for 1 (Fig. 1) and the HOMO for 15. In the HOMO of 15 the π orbital and the p orbital on



15: X = O, NCH₃

the oxygen are out of phase (negative overlap *cf* Fig. 4a). In the second highest occupied orbital of 1, however, the π -orbital and the p orbital on sulfur are in phase (Fig. 1). Consider now the transition state arising from addition of a carbenium ion "syn" or "anti" to the bridge (see above). The "syn" transition state of 15 shows additional stabilization (Fig. 4a) due to the in-phase overlap of the empty p orbital of the carbenium ion with both fragments of the " π " orbital. In the case of 1 the interaction between the " π " orbital and the empty 2p orbital of a carbenium ion does not lead to a similar stabilisation due to poor overlap.

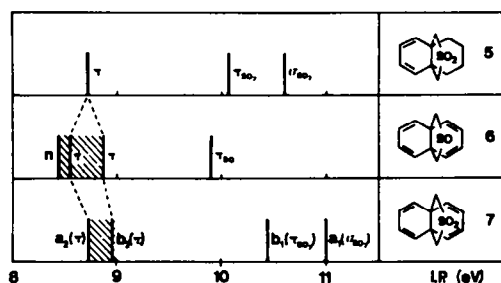


Fig. 3. Correlation of the first bands of the PE spectra of 5 to 7.

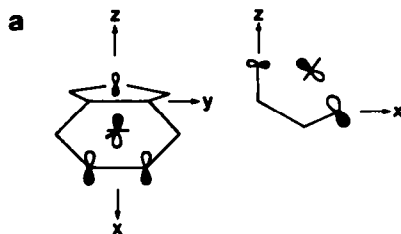


Fig. 4(a). Schematic representation of the phases in the HOMO of 15 and a carbenium ion adding to the double bond.

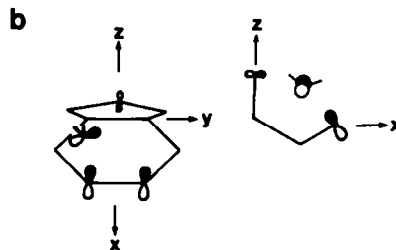


Fig. 4(b). Schematic representation of the phases in the HOMO of 1 and a carbene adding to the double bond.

For a carbene addition to 1 or 15 an unsymmetrical transition state is predicted.²⁰ Here a secondary orbital effect is operating only if the fragment orbitals interact in a bonding manner as realized in the " π " orbital of 1. A possible transition state for a carbene addition to 1 is shown in Fig. 4(b). Our argumentation is in line with experiments carried out by Ginsburg *et al.*²¹ They found

in epoxidation of 15 ($X=N-CH_3$) preferentially the syn product. For the ether 15 ($X=O$) the ratio syn:anti is 1:1.²¹ For carbenes it was found that 15 ($X=NMe$) adds more anti than syn.²²

EXPERIMENTAL

The compounds 1 to 7 were prepared according to the prescriptions in the literature.²³ The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield) equipped with a heated probe. The recording temp. was 80–110°. The spectra were calibrated with argon and a resolution of about 20 meV on the argon line was obtained. Each spectrum was recorded several times to ensure the reproducibility of the results.

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