Gas Phase ESCA Studies of 2,5-Diaza-1,6-dioxa-6a-thiapentalene and Its Selenium and Tellurium Analogues

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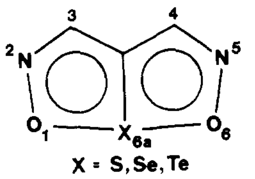
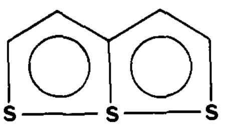
Abstract: 2,5-Diaza-1,6-dioxa-6a-thiapentalene and its selenium and tellurium analogues have been studied in the gas phase by means of ESCA. The effects of substitution in the 6a position have been studied for all nonhydrogen atoms in the molecule. The vibrational broadening of the O 1s lines is related to the observed bond lengths within a simple model.

Introduction

The 2,5-diaza-1,6-dioxapentalenes (I) may be regarded as derivatives of the well-known 1,6,6a-trithiapentalene system (II). Numerous experimental and theoretical studies have been undertaken in order to investigate the bonding properties of the linear three-sulfur sequence.[2a] Theoretical calculations,[2b] electron diffraction,[3] and more recently ESCA studies of II[4] have established that the potential-energy curve for the S-S-S system has a very flat minimum around the S-S equilibrium distance. In the S 2p spectra of II this property is revealed as an exceptionally broad S 2p line from the terminal sulfur atoms due to vibrational broadening.



(I)



(II)

In the present study we will investigate the bonding properties in the pentalene series (I) more thoroughly. From an ESCA point of view the molecules constitute an interesting series. As can be seen from the structural formulas of the systems I, the molecules contain four different nonhydrogen atoms in an aromatic 10π-electron system. The effects on these surrounding atoms when changing the element in the central (6a) position can thus be studied.

In the O-X-O sequence we have the unusual three-center bonds characteristic for trithiapentalene derivatives. Our study will therefore be particularly focused on the atoms in this sequence. Through the observation of vibrational broadening of core electron lines, we will try to elucidate the nature of the O-S-O potential curve and establish how this curve is affected by substituting the S_{6a} with Se and Te.

Each of these compounds has sufficiently high vapor pressure to allow their gas-phase ESCA spectra to be recorded. The resolution is thereby increased and calibration problems are reduced. As in a previous paper[4] the experiments are supplemented by CNDO/2 calculations as an aid in the interpretation of the recorded data.

Experimental Section

The core electron spectra were recorded by the electrostatic gas-phase ESCA instrument in Uppsala. This instrument uses a fine-focusing X-ray monochromating system and multichannel detection.[5]

The samples were generously supplied by Vialle[6] and used without further purification. The thiapentalene compound has a fairly high vapor pressure, and spectra with sufficient statistics were obtained at room tempterature. To achieve a sufficiently high vapor pressure for the selenium and tellurium compounds, the sample compartment was heated to 40 and 60 °C, respectively.

The spectra were calibrated by mixing the sample with a suitable calibration gas and by recording simultaneously the sample and calibration lines. This enables an absolute determination of the binding energies relative to the vacuum level. The following standard lines were used: O 1s (CO_2) 541.28 ± 0.12,[7] N 1s (N_2) 409.93 ± 0.10,[7] C 1s (CO_2) 297.69 ± 0.14,[7] Ar 3s 29.24,[8] and S $2p_{3/2}$ (SF_6) 180.27 ± 0.08 eV.[4]

Results and Discussion

Figure 1 shows the S 2p, C 1s, N 1s, and O 1s spectra obtained for 2,5-diaza-1,6-dioxa-6a-thiapentalene. The corresponding calibration lines are included for comparison.

The measured core electron binding energies for the S, Se, and Te compounds are listed in Table I. Note that there are two nonequivalent carbon atoms (C_3, C_{3a}) in the pentalene ring. The corresponding C 1s binding energies, however, almost coincide and cannot be resolved within the instrumental resolution. Nevertheless, an effect on the line width is observed, as will be discussed below. The $C_{3,3a}$ values listed in Table I correspond to the centroids of the peaks.

The $O_{1,6}$ binding energy is 4 eV smaller than the O 1s binding energy in O_2, which to a first approximation indicates quite a large negative charge on the oxygen atoms. The S_{6a} 2p electron lines are shifted 1.9 eV toward larger binding energy compared with the S_{6a} 2p lines of trithiapentalene.[4] In a qualitative sense this indicates a strong polarization of the O-S-O bonds relative to the S-S-S bonds, as may have been expected from electronegativity considerations.

It is also interesting to investigate the chemical shift of the various atoms when sulfur in the 6a position is substituted by selenium and tellurium. These chemical shifts, which are included in Table I, are small but with a clear trend. The monotonic decrease in the O 1s, C 1s, and N 1s binding energies when going from the sulfur to the tellurium compound is clearly seen in Figure 2. To a first approximation this may be interpreted as a flow of electron density from the 6a position to the rest of the molecule as the sulfur is substituted by consecutively less electronegative atoms. This trend is in accordance with the delocalized electron transport taking place in aromatic systems; see, e.g., the chemical shifts of benzene derivatives in ref 9.

The observed O 1s shifts indicate an increase of the ionicity of the O-X-O bonds when going from sulfur to tellurium.

Charge Distribution and Chemical Shifts. CNDO/2 calculations have been performed for all three molecules. The geometric parameters were taken from X-ray crystallographic studies[10] except for the hydrogen atoms, which were placed 1.08 Å from the $C_{3,4}$ atoms and with the C-H bonds bisecting the $N_{2,5}C_{3,4}C_{3a}$ angles. Since the Te structure could not be

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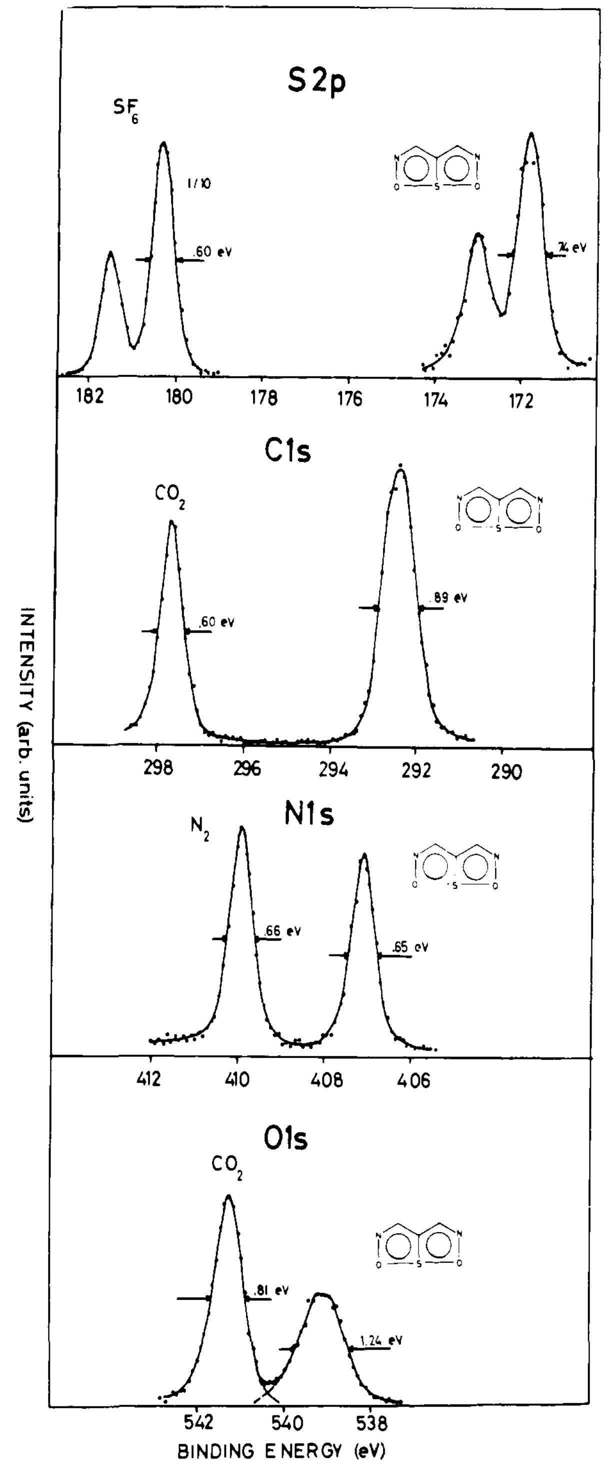

Figure 1. Core electron spectra for the thiapentalene compound.

corrected for thermal liberation,[10] uncorrected bond lengths are used for all three molecules. The molecular structures exhibit C_{2v} symmetry within the error limits, and the arithmetic mean of the two five-membered rings was used. For H, C, N, O, S, and Se the CNDO/2 parameters inherent in the program were employed.[11,12] The calculations involving Te were performed on a CNDO/2 program written by Manne[13] and with parameters estimated by Faegri.[14]

Slater's rules give very small and unrealistic orbital exponents for heavy elements when compared to those by Clementi and Raimondi.[15] Their optimized orbital exponents for S 3p and Te 5p were used to scale the Slater-rule value for S. Thus we obtained the orbital exponent 2.15 for the Te 5s, 5p and 5d orbitals (spd basis set).

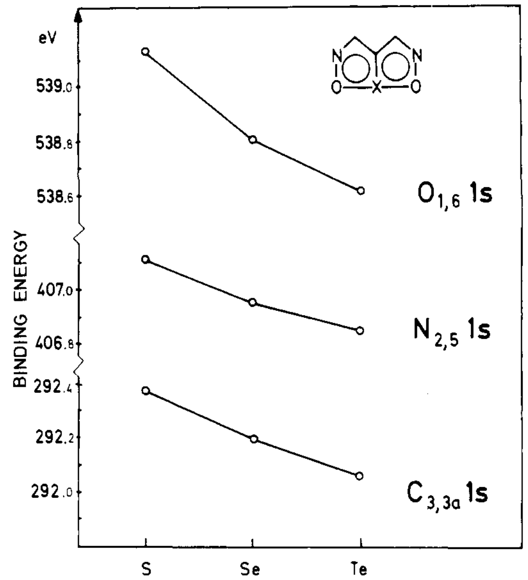

Figure 2. Variation of core electron binding energies with substitution in the 6a position.

Table I. Experimental Gas-Phase Core Electron Binding Energies[a] and Chemical Shifts (eV)

molecule	$O_{1,6}$	$N_{2,5}$ 1s	$C_{3,3a}$ 1s[b]	X_{6a}[c]
X = S	539.13	407.11	292.38	171.77
	0.0	0.0	0.0	
X = Se	538.81	406.95	292.20	63.88
	−0.32	−0.16	−0.18	
X = Te	538.62	406.85	292.06	581.49
	−0.51	−0.25	−0.32	

[a] Estimated error: ±0.05 eV. [b] The nonequivalent C_3 1s and C_{3a} 1s peaks could not be resolved. [c] The values correspond to the S $2p_{3/2}$, Se $3d_{5/2,3/2}$ (centroid binding energy), and Te $3d_{5/2}$ lines, respectively.

The resulting charge distribution is shown in Table II. The σ and π electron density components are also included. Except for the 6a position, there is only small variation of charge. It is interesting to note the redistribution taking place in the σ and π orbitals upon substitution. In the O-X-O sequence in particular, the decrease in σ density on X_{6a} is paralleled by an increase on the nearest neighbors and vice versa for the π density. The high π density on X_{6a} is mainly due to a pπ lone-pair formation that seems to increase when going from S to Te.

The sensitivity of the results with respect to variations in the parameters was tested with calculations using sulfur parameters for Se and Te, changing only the main quantum number. In spite of this radical substitution, the basic trends remained the same. This indicates that the parametrization errors are of no great consequence as long as the study is limited to chemical-shift effects on other atoms than the X_{6a} heavy element.

Ab initio calculations have also been performed on the thiapentalene compound.[16] The resulting charge distribution is dominated by the large electronegativity of the NO groups. This leads to a remarkably strong polarization of the molecule compared to the CNDO/2 results.

Electron binding energies may be estimated from the charge distribution by using the ground state potential model (GPM):[17]

$$E^G_{A\mu} = k^G_{A\mu} q^G_A + V^G_A + l^G_{A\mu} \qquad (1)$$

Here $E^G_{A\mu}$ is an approximation to the binding energy of subshell μ of the atom A, $V^G_A = \sum_{B\neq A} q^G_B / R_{AB}$ is the molecular po-

Table II. Charge (q) and Electron Density Distribution in σ and π Orbitals According to CNDO/2 Calculations

	X_{6a}			$O_{1,6}$			$N_{2,5}$			$C_{3,4}$			C_{3a}		
molecule	q	σ	π	q	σ	π	q	σ	π	q	σ	π	q	σ	π
S	0.15	4.08	1.77	−0.21	4.48	1.73	0.07	4.06	0.87	0.01	2.89	1.10	0.09	3.08	0.82
Se	0.20	3.99	1.81	−0.22	4.50	1.72	0.07	4.07	0.86	0.00	2.89	1.11	0.07	3.12	0.82
Te	0.26	3.85	1.90	−0.23	4.53	1.70	0.08	4.12	0.80	−0.02	2.89	1.13	0.06	3.14	0.80

Table III. GPM[a] and RPM[b] Calculations of Chemical Shifts in the CNDO/2 Approximation Compared with Experimental Results

	O 1s			N 1s			C_3 1s		C_{3a} 1s		$C_{3,3a}$ 1s[c]		
molecule	ΔE GPM	ΔE RPM	ΔE EXP	ΔE GPM	ΔE RPM	ΔE EXP	ΔE GPM	ΔE RPM	ΔE GPM	ΔE RPM	ΔE GPM	ΔE RPM	ΔE EXP
S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Se	−0.15	−0.30	−0.32	−0.10	−0.57	−0.16	−0.26	−0.47	−0.39	−0.53	−0.30	−0.49	−0.18
Te	−0.48	−0.93	−0.51	−0.06	−1.36	−0.26	−0.61	−0.97	−0.72	−0.75	−0.64	−0.90	−0.32

[a] GPM = ground state potential model. [b] RPM = relation potential model. [c] Centroid chemical shifts.

tential at atom A, $k^{G}_{A\mu}$ is a Coulomb repulsion integral between subshell μ and a suitable valence orbital on atom A, and $l^{G}_{A\mu}$ is a constant and can be disregarded when only shifts are calculated. It should be noted that this model does not include any relaxation effects, since only ground-state properties are used in the calculation. Using the theoretical k value as above gives an approximation to the Koopmans' value for the binding energy, i.e., the negative of the orbital energy eigenvalue of the ground-state Fock operator.

In order to include relaxation in the model we used the approach of Liberman[18] and Hedin and Johansson,[19] where separate calculations are made for the final and initial states. If $\epsilon^{G}_{A\mu}$ and $\epsilon^{I}_{A\mu}$ are orbital eigenvalues for the ground and ionized states, respectively, the binding energy is approximated by

$$E^{B}_{A\mu} = -\frac{1}{2}(\epsilon^{I}_{A\mu} + \epsilon^{G}_{A\mu}) \tag{2}$$

or equivalently, in terms of the relaxation energy

$$E^{rel}_{A\mu} = -\frac{1}{2}(\epsilon^{G}_{A\mu} - \epsilon^{I}_{A\mu}) \tag{3}$$

The negative of the orbital eigenvalues was approximated from potential model calculations, using the equivalent core ($Z + 1$) model to obtain the quantities used in the ion states:

$$E^{I}_{A\mu} = k^{I}_{A\mu} q^{I}_{A} + V^{I}_{A} + l^{I}_{A\mu} \tag{4}$$

$$E^{B}_{A\mu} = \frac{1}{2}(E^{I}_{A\mu} + E^{G}_{A\mu}) \tag{5}$$

$$E^{rel}_{A\mu} = \frac{1}{2}(E^{G}_{A\mu} - E^{I}_{A\mu}) \tag{6}$$

This will be referred to as the relaxed potential model (RPM).[20]

Experimental chemical shifts and the results from the GPM and RPM calculations for O, N, and C 1s levels are shown in Table III. The shifts are given relative to thiapentalene. The experimental trend, a monotonously varying substituent shift of about the same size on all core levels, is well reproduced by the RPM as well as the GPM model, the only discrepancy being the N 1s shift for the tellurium compound as calculated with the GPM.

The RPM seems to overestimate the shifts for all levels. This has previously been found to be an effect of the minimal basis set employed in CNDO/2 calculations.[21] However, even small trends within a series of related compounds were found to be correctly reproduced, owing to the cancellation of systematic approximation errors.

The C_3 1s and C_{3a} 1s electron lines could not be distinctly separated. Therefore the centroid chemical shifts are included in Table III.

Table IV. Theoretical Binding Energy Difference C_{3a} 1s − C_3 1s Compared to the Experimental C 1s Width[a]

molecule	ΔE GPM	ΔE RPM	fwhm exp
S	0.91	0.57	0.89
Se	0.78	0.51	0.70
Te	0.79	0.80	1.16

[a] Owing to charging of the sample compartment it is impossible to obtain a good spectrometer line profile and therefore the statistics do not permit a detailed deconvolution of the two C 1s peaks. A rough estimate based on line broadening,[17] however, gives energy differences between the C_{3a} 1s and C_3 1s lines of 0.6 ± 0.2, 0.3 ± 0.2, and 0.7 ± 0.2 eV for the S, Se, and Te compounds, respectively.

As seen in Figure 1, the C 1s lines are rather broad and a large variation of the line widths was observed for different elements in the 6a position. The variation of the line widths could in principle be explained by three different mechanisms: (a) a variation of the natural line widths; (b) a vibrational broadening effect; (c) a variation of the chemical shifts of the two unresolved line components.

Since the C 1s natural line width is less than 0.1 eV it is impossible to detect any variations of this quantity within the spectrometer resolution. In order to elucidate to what extent mechanism (b) contributes to the variation of the line widths it is possible to make a comparison with C 1s lines in other aromatic ring systems. An extensive study of this type was made in, e.g., ref 9 where no effects could be detected which were of the order of magnitude found here.

Therefore explanation (c) remains most probable. We may discuss this in detail using the CNDO/2 results. The experimental fwhm of the C 1s line, as seen in Table IV, first decreases when S is substituted by Se and increases when Se is substituted by Te. The spectrometer resolution was fairly constant, as can be seen from the fwhm's of the reference lines given in Table V.

There are two possible variations of the C_3 1s and C_{3a} 1s chemical shifts that could explain the observed trend in the fwhm's.

(1) The change in the C_3 1s and the C_{3a} 1s shifts may go in the opposite directions for a consecutive substitution of S by Se and Te in such a way that the relative line positions are reversed.

(2) The C 1s shifts do not vary monotonically when substituting S by Se and Te.

As seen from the difference in calculated C_3 1s and C_{3a} 1s chemical shifts of Table IV, the relaxation potential model supports the latter explanation. A comparison of the differences $E_{GPM} - E_{RPM}$ indicates that the relaxation energies are increasing for all elements when the heavier elements Se and Te substitute S in the 6a position. An exception occurs for the

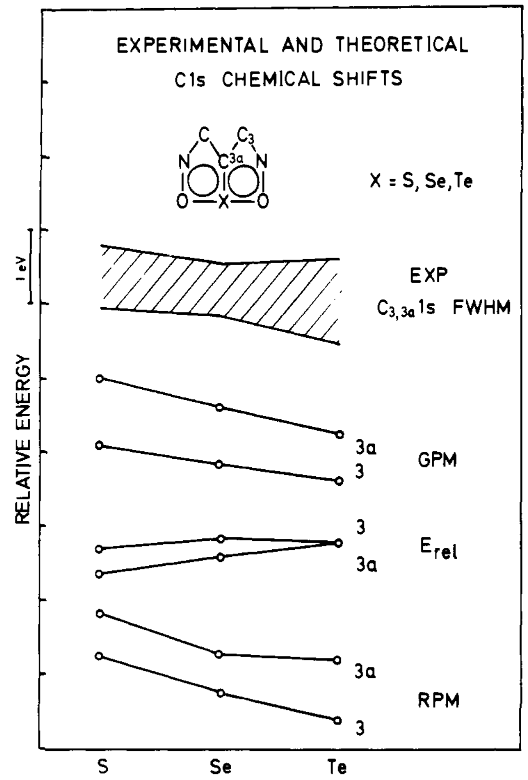

Figure 3. Theoretical ground-state and final-state contributions to the C_3 1s − C_{3a} 1s binding energy difference compared to the experimental C 1s width. For definitions of E_{GPM}, E_{rel}, and E_{RPM}, see (1), (5), and (6). $E_{RPM} = E_{GPM} - E_{rel}$.

C_{3a} 1s ionization which gives the largest calculated relaxation energy for Se. The results of the GPM and RPM calculations are summarized in Figure 3 together with the experimental C 1s line widths. Note that the difference in C_3 1s and C_{3a} 1s line positions only in a qualitative way can be compared with the experimental line widths.

It should be mentioned in this connection that these last results for the Te compound depend somewhat on the orbital exponents chosen. Trial calculations have shown that the relaxation energy of the C_{3a} 1s line will increase when smaller exponent values are used, and will eventually result in a negative C_{3a}-C_3 shift. The possibility of an energy inversion of the C_3 and C_{3a} 1s lines, explaining the variation of the observed fwhm, cannot therefore be completely ruled out.

It should also be mentioned that the calculated shifts to some extent depend on the geometrical parameters. For the Se and in particular the Te compound, the error limits are large. In fact, an analysis of bond lengths and bond angles shows that the Se and Te molecular structures within the error limits may be constructed from the more accurate S structure. This is simply done by increasing the $O_1N_2C_3$, $N_2C_3C_{3a}$, and $C_3C_{3a}S_{6a}$ bond angles 1.2 and 2.1°, respectively, and adjusting for the different C_{3a}-X_{6a} bond lengths.[22] Calculations based on these "constructed" molecules were performed in order to test the dependence on geometric parameters. However, the calculated shifts show no substantial change in the overall results and trends.[22]

Vibrational Broadening and the O-X-O Bonds. The O 1s electron line of the thiapentalene compound is observed to be very broad; see Figure 1. This is in agreement with the $S_{1,6}$ 2p spectra of trithiapentalene.[4] In the latter case the S_{6a} 2p peaks overlapped and deconvolution was necessary. For the compounds in this study the lines in the O-X-O sequence do not overlap and the interpretation is facilitated. The relatively narrow S_{6a} 2p lines observed for thiapentalene are in agreement with the deconvoluted S_{6a} 2p lines in trithiapentalene which confirms the earlier assignments. As discussed earlier[4] the broad $S_{1,6}$ 2p lines are the result of an extensive vibrational broadening. This effect may be explained on the basis of a very flat ground state potential curve and a substantial change in the S-S distance upon ionization.

Table V. Observed and Corrected Line Widths (eV) for the C, N, and O 1s Lines

molecule	atom	fwhm = A^a	fwhm = R^b	$B = \sqrt{A^2 - (R^2 - R_1^2)}^c$
	C 1s	0.89	0.60	0.89
S	N 1s	0.65	0.66	0.64
	O 1s	1.24	0.81	1.19
	C 1s	0.70	0.62	0.68
Se	N 1s	0.66	0.65	0.66
	O 1s	1.08	0.73	1.08
	C 1s	1.16	0.66	1.13
Te	N 1s	0.69	0.67	0.67
	O 1s	0.89	0.74	0.88

[a] Full width at half-maximum for the atom studied. [b] Full width at half-maximum for the reference atom. [c] Line widths corrected relative to the narrowest reference atom R_1 of each series.

Table V shows the line widths for the C, N, and O 1s lines for the S, Se, and Te compounds. The first two columns compare the fwhm for the studied atom and the reference atom, respectively. The widths of the reference lines have been used to correct for the variation in instrumental broadening. The corrected line widths relative to the narrowest reference atom of each series are displayed in the third column of Table V. The C 1s lines are broadened because of the nonequivalent carbon atoms in the molecules as discussed above. It is interesting to note that the N 1s lines are not significantly broadened, especially when compared to the O 1s lines. Ionization of a N 1s electron seems to affect the bonding in the molecule very little compared to ionization of an O 1s electron.

The most interesting feature of Table V is, however, the decrease in vibrational broadening for the O 1s line when going from the sulfur to the tellurium compound. The change in the experimental line width is close to 0.4 eV. The question now arises if this variation in vibrational broadening could be related to structural and bonding parameters.

In order to discuss this we may reexamine the trithiapentalene results and try to determine the factors that are of importance for the fwhm of the core electron lines from the elements in the 1,6 position. The results of the CNDO/2 calculations displayed in Figure 4 may be interpreted in a very simple model. If we first regard the ground-state potential for the "bell clapper" motion of the S_{6a} atom we may conclude that it can be decomposed into two more or less distinct regions: (I) an approximately 0.35 Å wide region centered around the ground-state equilibrium of the S_1-S_{6a} bond distance of 2.35 Å (the potential is here very flat; the forces between the atoms are here probably caused by the rather weak three-center bonds); (II) the regions outside region I where the potential is strongly repulsive and probably reflects the forces between two sulfur atoms in close contact. It should be noted that the limit between I and II is close to the S_1-S_{6a} distance of 2.10 Å, which is equal to the S-S single bond length.[23]

Since the ground-state potential of trithiapentalene is very flat the splitting between the vibrational energy levels is very small, in the order of a few hundredths of an electronvolt. Therefore we may conclude that *the vibrational amplitude in the ground state is mainly determined by the width of region I.*

When ionizing the S_1 atom the CNDO/2 calculations indicate that the minimum of the potential curve is moved strongly toward the S_6 atom. In this simple picture we may say that the three-center bond seems to be strongly perturbed and

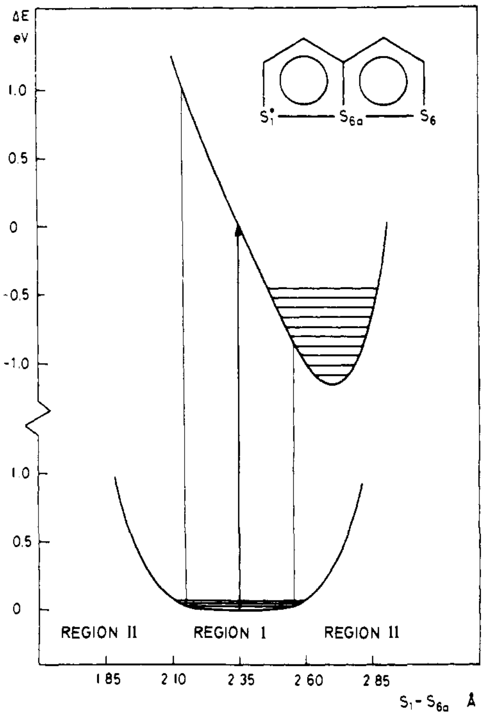

Figure 4. Ground-state and final-state potential curves for trithiapentalene as found from CNDO/2 calculations and the equivalent core approximation (from ref 4).

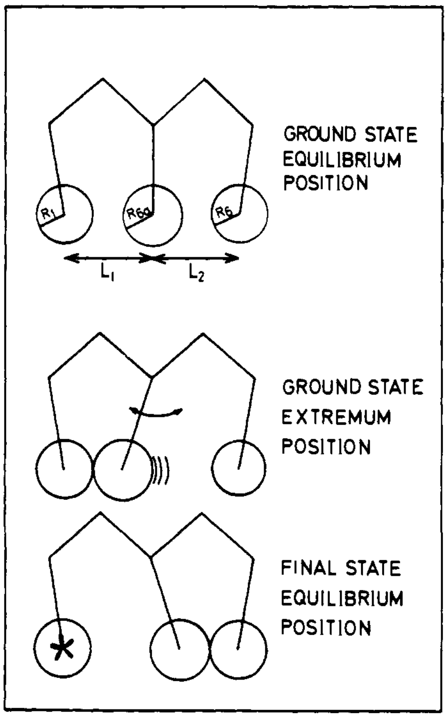

Figure 5. Schematic description of the geometrical parameters which are used to describe the vibrational broadening for an ionization in a terminal atom.

a repulsive force between the ionized S_1 atom and the S_{6a} atom moves the latter away. Equilibrium is reached when the forces between the S_{6a} and S_6 atoms become repulsive enough. For the further discussion it is sufficient to conclude that the potential minimum of the final state lies somewhere outside region I, and we may as earlier approximate the final state potential curve in region I by a straight line.[4]

The discussion above is schematically illustrated in Figure 5. With the approximations made the fwhm of the vibrationally broadened electron line from an element in the 1,6 positions may be calculated easily as a simple product[4,26]

$$\text{fwhm} = k_s\,(\mathrm{d}E_f/\mathrm{d}x)_{x=x_0}\,\Delta X_G \qquad (7)$$

where $(\mathrm{d}E_f/\mathrm{d}x)_{x=x_0}$ is the slope of the final state potential curve at the equilibrium position for the ground-state vibrational motion, ΔX_G is the ground-state vibrational amplitude, and k_s is a parameter that depends on the line shape and the approximations involved when the slope and amplitude are estimated. In the light of the discussion above, ΔX_G may be approximated (see Figure 5) as

$$\Delta X_G = L_1 + L_2 - 2R_{6a} - R_1 - R_6 \qquad (8)$$

where L_1 and L_2 are the bond lengths between the atoms in the 1 and 6a and the 6 and 6a positions, respectively. R_1, R_6, and R_{6a} are estimates of the appropriate "atomic bond radii". In the present case

$$\Delta X_G = 2(L - (R_{6a} + R)) \qquad (9)$$

since $L_1 = L_2 = L$ and $R_1 = R_6 = R$. The most obvious choice of estimates of the atomic bond radii is of course the covalent single bond radii. According to (9) ΔX_G is then approximated as twice the difference between the observed O–X bond length and the corresponding O–X single bond. However, in choosing the approximate single-bond radii for S, Se, and Te one must be careful. The Pauling covalent radii for these atoms[24] were obtained by averaging over a few different molecules and may not apply directly to our systems. Ideally one should be able to deduce the single-bond radii from a constant property inherent in the structures. One such property may be the C_{3a}–X_{6a} bond lengths. (It has been shown for trithiapentalene derivatives with no molecular strain that the C_{3a}–S_{6a} bond lengths remain remarkably constant for a great variety of different S_1–S_{6a} and S_{6a}–S_6 bond lengths.[25] A consistent set of single-bond radii for S, Se, and Te may then be calculated from the S molecular structure if one assumes that the bond-length decrease relative to the corresponding single bond remains constant for these compounds:

$$\frac{(R_{3a} + R_{6a}) - (C_{3a}\text{–}X_{6a})_{\text{obsd}}}{R_{3a} + R_{6a}} = k \qquad (10)$$

With the accepted single-bond radii R_{6a} = 1.05 Å[23] for S and R_{3a} = 0.77 Å[24] for C, the obtained k value may be used to deduce R_{6a} for Se and Te. The observed C_{3a}–X_{6a} values are 1.67, 1.81, and 1.98 Å, respectively, for X_{6a} = S, Se, and Te.[10] Thus the single-bond radii for Se and Te obtained from (10) are 1.20 and 1.39 Å, respectively. For the smaller oxygen atom we have used R = 0.66 Å.[24]

The next parameters to be estimated in (7) are the slopes of the final state potential curves, $(\mathrm{d}E_f/\mathrm{d}x)_{x=x_0}$. These slopes cannot be obtained from structural data alone. We may as a first approximation choose the slope for trithiapentalene from Figure 4, $(\mathrm{d}E_f/\mathrm{d}x)_{x=x_0}$ = 4.5 eV/Å.

From (7) it follows that the fwhm's are proportional to $(\mathrm{d}E_f/\mathrm{d}x)_{x=x_0}\Delta X_G$ provided that the line shapes are fairly constant, and in Table VI this quantity is compared with the observed line widths for O 1s. The agreement is good except for Te, as can be seen when k_s is calculated from the observed fwhm's.

The Te discrepancy may be understood from the fact that the O–Te–O bonds are unusually short for a trithiapentalene derivative. They are only 2% longer than the corresponding covalent single bonds. This makes ΔX_G very small and, as mentioned above, our model may not apply. The percent elongations for the Se and S compound are 5.6 and 7.6%, respectively, and as much as 12% for trithiapentalene.

The elongation relative to the corresponding single bond is mentioned because this quantity has been used[1] as a measure for bond strength, or more correctly bond "weakness", for

Table VI. Comparison of Observed O 1s Line Widths and Line Widths Calculated from the Simple Model:

$$\text{fwhm} = k_s(dE_f/dx)_{x=x_0}\Delta X_G$$

X_{6a}	obsd[a] O-X, Å	ΔX_G, Å[b]	$(dE_f/dx)_{x=x_0} \cdot \Delta X_G$, eV[c]	obsd[d] fwhm	k_s[e]
S	1.84	0.26	1.17	1.19	1.0
Se	1.98	0.24	1.08	1.08	1.0
Te	2.09	0.08	0.36	0.88	2.4

[a] The bond lengths are not corrected for libration. [b] Calculated as twice the difference between the observed O-X bond length and the corresponding single bond. [c] Assuming $(dE_f/dx)_{x=x_0} = 4.5$ eV/Å. [d] Corrected line widths relative to the narrowest reference atom; see Table V. [e] Calculated from the observed fwhm's.

Table VII. Observed and Estimated O 1s Line Widths from CNDO/2 Calculations and the Model:

$$\text{fwhm} = k_s(dE_f/dx)_{x=x_0}\Delta X_G$$

X_{6a}	ΔX_G, Å	$(dE_f/dx)_{x=x_0}$, eV/Å	$(dE/dx)_{x=x_0} \cdot \Delta X_G$, eV	obsd[a] fwhm, eV	k_s[b]
S	0.117	6.2	0.73	1.19	1.6
Se	0.081	5.4	0.44	1.08	2.5
Te	0.077	4.3	0.33	0.88	2.7

[a] Corrected for variation of the instrument resolution; see Table V. [b] Calculated from the observed fwhm's.

trithiapentalene derivatives. In our notation the expression is

$$B = \frac{1}{2}\frac{\Delta X_G}{(R + R_{6a})}100\% \tag{11}$$

where $(R + R_{6a})$ represents the single bond length. The connection with the fwhm expression is readily seen.

The fwhm of the O 1s lines may also be estimated directly from CNDO/2 calculations. Potential-energy curves for the ground and final states have been calculated for the "bell-clapper" motion of the X_{6a} atom. As before[4] the displacement of the central atom was performed within a fixed molecular framework. This assumption is consistent with the electron diffraction analysis of trithiapentalene.[3]

The width ΔX_G in (7) may then be calculated from the ground-state vibrational wave function in the harmonic oscillator approximation.[26] This width is proportional to the width of the potential at the zero-point energy, and we have used the latter quantity as ΔX_G in (7) to maintain the analogy to the discussion above.

Table VII shows the results of the calculations. From the relatively small ΔX_G values it follows that the ground-state potentials for all three molecules come out considerably more narrow than for trithiapentalene. Furthermore, the slopes of the final state potential curves are not constant, but decrease somewhat as ΔX_G decreases. However, in spite of all the approximations involved, the observed trend is fairly well reproduced also in this case. The deviation for Se may be due to the small (Slater's rule) orbital exponent used, as the potential curves depend strongly on these exponents.

When our qualitative "structural" model was applied above, we assumed constant slopes $(dE_f/dx)_{x=x_0}$. The CNDO/2 calculations suggest that they may be different. This implies that one must be careful when structural data alone are used in the model.

The relation between bonding parameters and ESCA line widths, discussed within this simple model, applies also to other pentalenes. This will be discussed in a forthcoming paper.

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