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Solid-State ESCA Studies of Trithiapentalene and Selenium Analogues

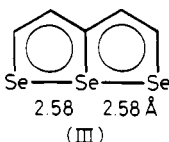
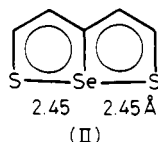
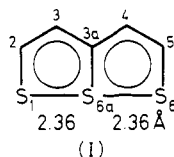
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1,6,6a-Trithiapentalene (I), 1,6-dithia-6a-selenapentalene (II), and 1,6,6a-triselenapentalene (III) have been studied in the solid state by means of ESCA. Careful sample preparation made it possible to obtain an S 2p spectrum comparable to that of trithiapentalene in the gas phase and to compare the line widths of the core hole states for the atoms in the 1,6 and 6a positions. The vibrational broadening of the S 2p and Se 3d lines from the terminal 1,6 atoms is related to the observed bond lengths within a simple model. The results indicate more narrow ground-state potential curves for the Se derivatives than for trithiapentalene, a conclusion supported by the results from structure studies and CNDO/2 calculations.

Introduction

X-ray crystallographic studies of 1,6,6a-trithiapentalene (I),² 1,6-dithia-6a-selenapentalene (II),^{3a} and 1,6,6a-triselenapentalene (III)^{3b} show that the molecules possess C_{2v} symmetry within the experimental errors. The S-S, S-Se, and Se-Se bond lengths are all longer than the corresponding single bonds, suggesting a special type of bonding in these molecules.⁵



Gas-phase ESCA studies of I show very broad S 2p lines from the terminal sulfur atoms due to vibrational broadening, which indicates a very "flat" energy minimum around the S-S equilibrium distance.⁴ This is consistent with other experimental and theoretical findings,^{5,6} in particular with X-ray crystallographic results on substituted trithiapentalene derivatives, where the S-S bond lengths are found to vary within the range 2.16–2.50 Å.² An explicit relationship between structural parameters and core electron line widths has recently been proposed for a series of related oxygen compounds.⁷

The bonding properties of the selenium analogues II and III are much less established than for I. The object of the present work is to study the vibrational broadening for the atoms in the 1,6,6a three-center sequences of the molecules and to compare the broadening with structural parameters.

The low vapor pressure of compounds II and III made gas-phase measurements impractical, and all three molecules were studied in the solid phase. Since reliable line width values were required, special care was taken during sample preparation to exclude the possibility of inhomogeneous sample charging.

Experimental Section

The measurements were performed on a Hewlett-Packard 5950A ESCA spectrometer.⁸ The samples were generously supplied by Reid⁹⁻¹¹ and used without further purification. Thin films of the compounds were evaporated onto cooled backings of either gold or pyrolytic graphite in the preparation chamber of the spectrometer. The standard HP evaporation probe was slightly modified for this purpose. The compounds were introduced into the preparation chamber in a tiny glass tube surrounded by a tungsten coil. This arrangement enabled us to introduce samples with fairly high vapor pressure. An additional advantage of this arrangement was that only minor amounts of the compounds were needed.

The best results were obtained with a film thickness of a few hundred nanometers. Thinner films did not cover completely, and a subsequent decrease in the signal to background ratio was observed. For thicker films inhomogeneous sample charging occurred, and reproducible results could not be obtained. The floodgun was not used during measurements, and reasonable floodgun settings were not found to affect the spectra. The base pressure during evaporation was 10^{-6} Pa, and in the analyzing chamber the pressure was 10^{-7} Pa. All samples were measured at a temperature of about 170 K.

Results and Discussion

Trithiapentalene. The S 2p electron spectra of trithiapentalene (I) in the gaseous and solid state are shown in Figure 1. Compared to previous recordings,^{12,13} the quality of the solid-state spectrum is improved and is nearly as well resolved as the gas-phase spectrum. As before⁴ the best fit to the experimental data is obtained with one sharp and one very broad S 2p_{3/2,1/2} doublet. The deconvolution is performed without any assumption concerning line shapes but assumes that the intensity ratio is 1:2 for the S 2p doublet and that the components of each doublet have the same line width and line profiles.

The $S_{1-S_{6a}}$ chemical shift and the width of the terminal sulfur atoms are, within the experimental errors, found to be the same in the two phases. In the solid state, the $S_{6a}2p$ doublet lines are broadened due to the somewhat lower resolution.

The S 2p spectrum of I has been interpreted and discussed in detail earlier.⁴ The great similarity of the gas-phase and the solid-state spectra suggests that solid-state effects are small. In fact, calculation of the ground-state crystal potential contribution yields only a 0.1-eV change in the $S_{1-S_{6a}}$ chemical

(1) (a) University of Tromsø. (b) Uppsala University.
 (2) Hansen, L. K.; Hordvik, A. *Acta Chem. Scand.* **1973**, *27*, 411.
 (3) (a) Hordvik, A.; Julshamn, K. *Acta Chem. Scand.* **1971**, *25*, 1895. (b) *Ibid.* **1971**, *25*, 2507.
 (4) Saethre, L. J.; Svensson, S.; Mårtensson, N.; Gelius, U.; Malmquist, P. Å.; Basillier E.; Siegbahn K. *Chem. Phys.* **1977**, *20*, 431.
 (5) Hansen, L. K.; Hordvik A.; Saethre, L. J. In "Organic Sulphur Chemistry"; Stirling, D. J. M., Ed.; Butterworths: London, 1975; p1.
 (6) Gleiter, R.; Cygax, R. *Top. Curr. Chem.* **1976**, *63*, 49.
 (7) Saethre, L. J.; Mårtensson, N.; Svensson, S.; Malmquist, P. Å.; Gelius, U.; Siegbahn, K. *J. Am. Chem. Soc.* **1980**, *102*, 1783.

(8) Siegbahn, K.; Hammond, D.; Fellner-Feldegg, H.; Barnett, E. F. *Science* **1972**, *176*, 245.
 (9) (a) Dingwall, J. G.; McKenzie, S.; Reid, D. H. *J. Chem. Soc. C* **1968**, 2543. (b) Dingwall, J. G.; Reid, D. M.; Symon, J. D. *Ibid.* **1970**, 2412.
 (10) Reid, D. H. *J. Chem. Soc. C* **1971**, 3187.
 (11) Jackson, M. G.; Reid, D. H., unpublished results.
 (12) Lindberg, B.; Högberg, S.; Malmsten, G.; Bergmark, J.; Nilsson, Ö; Karlsson, S. E.; Fahlman, A.; Gelius, U.; Pinel, R.; Stavaux, M.; Mollier, Y.; Lozac'n, N. *Chem. Scr.* **1971**, *1*, 183.
 (13) Coffey, M. O. Thesis, Purdue University, 1972; University Microfilms, Ann Arbor, Michigan.

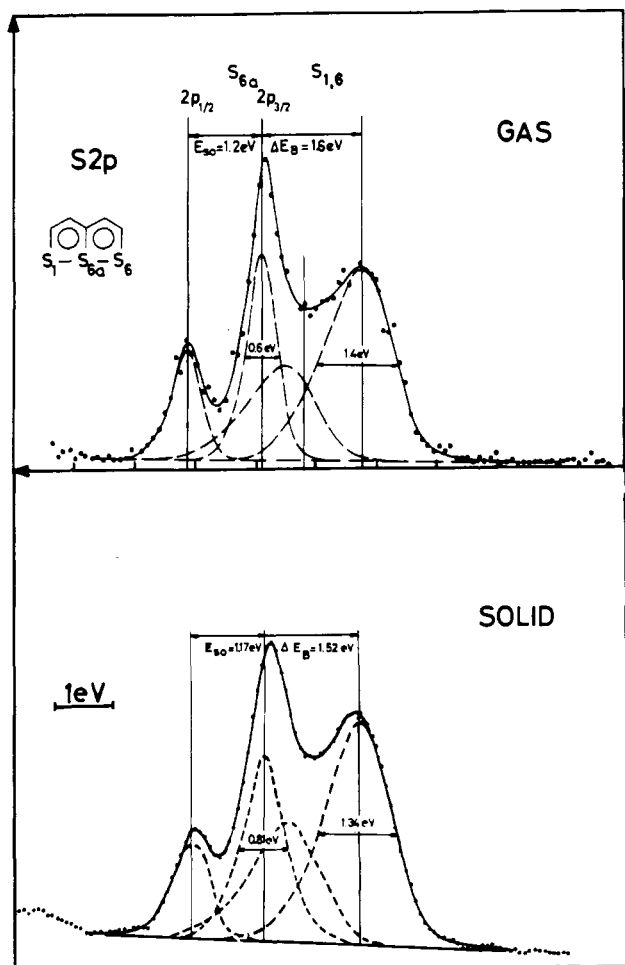


Figure 1. S 2p electron spectra of trithiapentalene in the gaseous and solid phase. The spin-orbit splitting (E_{SO}) and chemical shift between peak maxima (ΔE_B) are shown. The chemical shift from centroid vertical binding energies are found to be 1.5 eV for both phases (see Table I). The fwhm values of the 6a and 1,6 atoms are indicated.

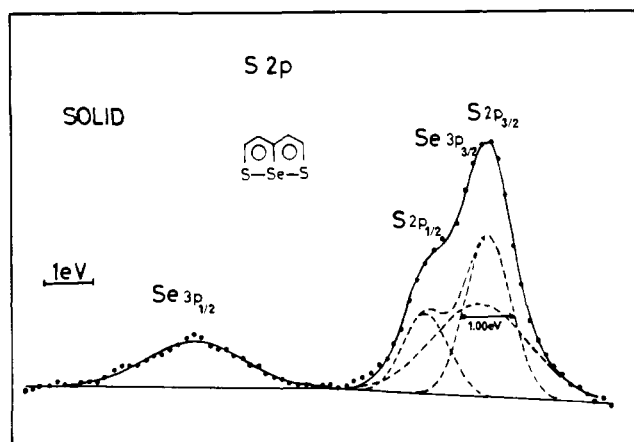


Figure 2. S 2p electron spectrum of dithiaselenapentalene in the solid phase. The S 2p spectrum interacts with the Se 3p spectrum. The fwhm for the S 2p line is indicated.

shift. The crystal potential was calculated from CNDO/2 atomic charges by using a computer program written by Busing.¹⁴

The $S_{1,6}$ 2p line widths of the two phases are also equal within experimental errors (see Figure 1), and the solid-state

Table I. Comparison of the Spin-Orbit Splitting (E_{SO}) Chemical Shift ($E_{6a} - E_{1,6}$) and Line Widths (fwhm) for the Atoms in the Three-Center Sequence 1, 6a, and 6^a

three-center sequence	phase	E_{SO}^b	$E_{6a} - E_{1,6}^c$	fwhm ^d	
				6a	1,6
S-S-S	gas	1.20 (5)	1.50 (5)	0.60 (5)	1.37 (5)
S-S-S	solid	1.17 (5)	1.52 (5)	0.81 (5)	1.34 (5)
S-Se-S	solid	1.20 (5)		0.85 (3)	1.00 (5)
Se-Se-Se	solid	0.88 (3)	1.15 (5)	0.83 (3)	0.97 (3)

^a The estimated errors given in parentheses refer to the last digits of the respective values (eV). ^b The values correspond to S ($2p_{3/2} - 2p_{1/2}$) and Se ($3d_{5/2} - 3d_{3/2}$). ^c Centroid vertical binding energies. ^d Full width at half-maximum.

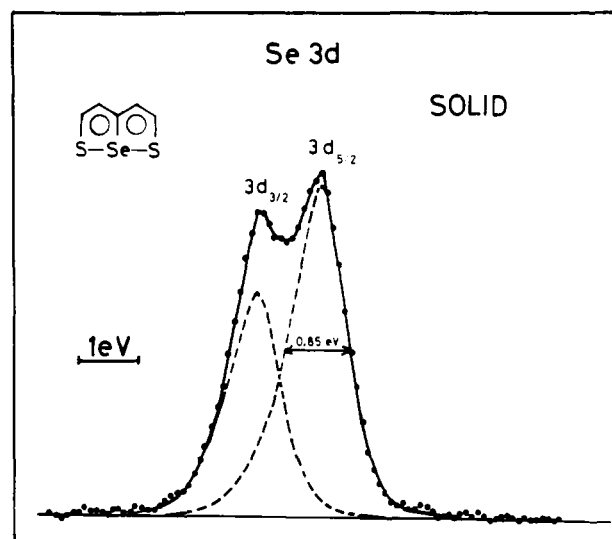


Figure 3. Se 3d electron spectrum of dithiaselenapentalene. The fwhm value is indicated.

line widths were obtained with good reproducibility. This implies that the desired trend study of the line widths can be performed with confidence in the solid state. The problem is of course simplified by the fact that only samples with similar physical properties are investigated here.

Dithiaselenapentalene. Figure 2 shows the solid-state S 2p spectrum of dithiaselenapentalene (II). Unfortunately this spectrum interacts with the Se 3p spectrum of the central 6a atom. This complicates the deconvolution, and the S 2p line width had to be determined by a numerical fitting procedure. The result is shown in Table I.

The Se 3d spectrum of II is shown in Figure 3. The spectrum was deconvoluted without any assumption concerning line shapes but with a fixed spin-orbit splitting of 0.88 eV obtained from a gas-phase measurement of the Se 3d line in 1,6-dioxo-2,5-diaza-6a-selenapentalene.⁷ The relatively narrow lines confirm the earlier assignment of the trithiapentalene spectrum, and, as seen below, the interpretation of the triselenapentalene spectrum is hereby simplified.

Triselenapentalene. The solid-state Se 3d spectrum of triselenapentalene (III) is shown in Figure 4. The deconvolution is performed in the same way as for I. Compared to the S 2p spectrum of I, the whole Se 3d spectrum appears a little compressed. This is due to the smaller spin-orbit splitting, vibrational broadening, and chemical shift between the central and terminal atoms in the three-center sequence. However, the overall features and assignment are very similar for I and III. Note that the fwhm's of the Se_{6a} 3d lines for II and III are equal within the experimental error.

When the $S_{6a}-S_{1,6}$ and the $Se_{6a}-Se_{1,6}$ chemical shifts for I and III are compared (see Table I), one should have in mind that the one-center electron-repulsion integral between a core

(14) Busing, W. R. Technical Report ORNL-4976; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1974; pp 154, 155.

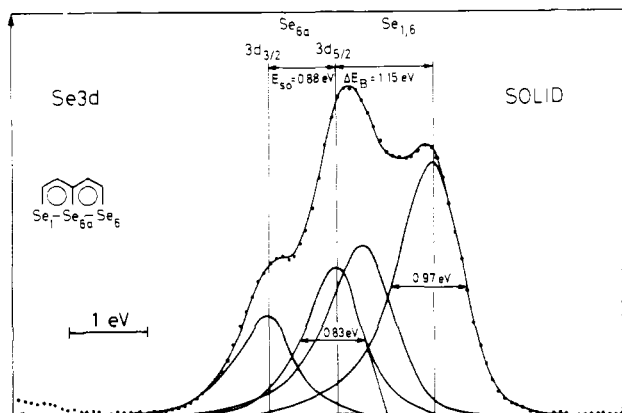


Figure 4. Se 3d electron spectrum of triselenapentale in the solid phase. The spin-orbit splitting (E_{SO}) and chemical shift between peak maxima (ΔE_B) are shown. The fwhm for the 6a and 1,6 atoms are indicated.

and a valence electron is smaller for Se than for S. This means that the shift will be smaller for Se even if the charge distributions were identical. This can easily be seen from the ground-state potential model¹⁵ (eq 1). The electron repulsion

$$\Delta E = k\Delta q + \Delta V \quad (1)$$

parameter k as calculated from standard CNDO input parameters is 22% smaller for Se than S.²⁴ This value may be compared to the 24% smaller shift observed for Se. The charge distribution in the three-center sequence is discussed below.

Vibrational Broadening and Bonding in the Three-Center Sequence. The experimental widths of the S 2p and Se 3d electron lines for I, II, and III are summarized in the last two columns of Table I. Within the estimated errors, the line widths of the atoms in the 6a position are equal for all compounds in the solid state. Thus there are only minor differences in the vibrational broadening for the 6a atoms when Se is substituted for S in II and III. Note also that the lifetime broadening of the S 2p and Se 3d lines is small compared to other broadenings effects.

It should be mentioned that it can be difficult to distinguish between vibrational broadening and other line-broadening effects in solid-state spectra. An estimate can, however, be made from the gas-phase spectrum of I, where the instrument resolution was continuously checked against the reference line. From that spectrum,⁴ it can be concluded that the amount of vibrational broadening for the central 6a atom is not larger than a few tenths of an electronvolt. The values obtained for the 6a atoms in the solid state are therefore probably close to the experimental resolution in this case.

The vibrational broadening of the 1,6 atoms are strongly affected by Se substitution; see Table I. The most probable interpretation of the decrease in observed line widths is that it reflects a change in the bonding properties of II and III compared to I.

As discussed earlier,^{4,7} the broad $S_{1,6}$ 2p lines for I are the results of an extensive vibrational broadening, explained on the basis of a very flat ground-state potential curve and a substantial change in the S-S distance upon core ionization. This is illustrated in Figure 5, which shows the result of CNDO/2 calculations of the ground- and final-state potential curves for I. On the basis of Figure 5, a simple model was recently⁷ proposed for the vibrational broadening (eq 2). Here

$$\text{fwhm} = k_s(dE_f/dx)_{x=x_e}\Delta X_G \quad (2)$$

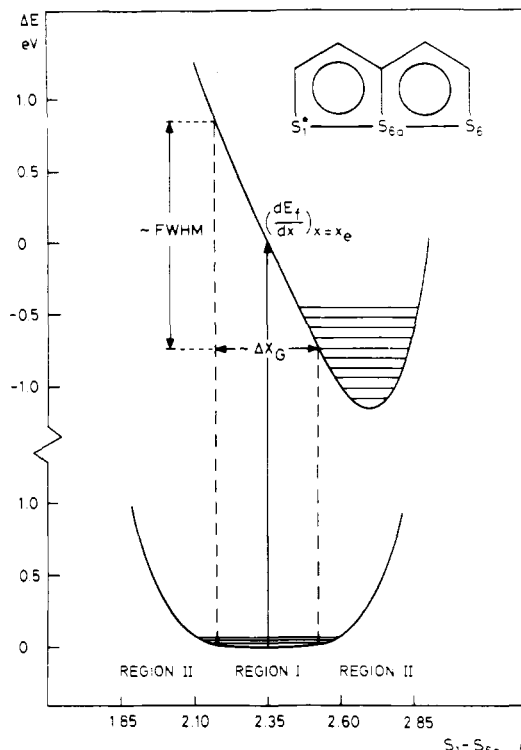


Figure 5. Ground- and final-state potential curves for trithiapentale as found from CNDO/2 calculations and the equivalent-core approximation (from ref 4).

Table II. Comparison of Observed ESCA Line Widths (fwhm) with Vibrational Amplitudes (ΔX_G) Estimated from Structural Data, Using the Simplified Line Width Model $\text{fwhm} = K\Delta X_G$

three-center sequence	L , Å	ΔX_G , ^a Å	obsd fwhm, ^b eV	K , eV/Å
S-S-S	2.36	0.52	1.34	2.6
S-Se-S	2.45	0.40	1.00	2.5
Se-Se-Se	2.58	0.36	0.97	2.7

^a Calculated as twice the difference between the observed 1-6a bond length and the corresponding single bond (see eq 3 in text).

^b These solid-state fwhm:s are uncorrected for spectrometer resolution. A direct comparison with the gas-phase values obtained in ref 7 can therefore not be made.

ΔX_G is the ground-state vibrational amplitude, $(dE_f/dx)_{x=x_e}$ the slope of the final state potential curve at the equilibrium position, and k_s a parameter which depends on the line shape and approximations involved. Since the vibrational amplitude ΔX_G is mainly determined by the width of region I (see Figure 5), ΔX_G may be approximated from structural data (eq 3).

$$\Delta X_G = 2(L - (R_1 + R_{6a})) \quad (3)$$

In eq 3 L is the 1-6a bond length, and R_1 and R_{6a} are the approximate single-bond radii for atoms 1 and 6a, respectively. A consistent set of S and Se single-bond radii was estimated as described earlier.⁷ It was assumed that the decrease in C_{3a} - Se_{6a} bond length relative to the single bond is the same as for C_{3a} - S_{6a} in I. Since the bond lengths in II and III have large error limits, the C_{3a} - Se_{6a} bond length, 1.90 Å, was obtained as an average of the six known structures with S-Se and Se-Se bonds.^{3,16,17} With $R = 1.05$ Å for S¹⁸ and 0.77

(15) Siegbahn, K.; Nordling, C.; Johansson, G.; Hedman, J.; Hedén, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Werme, L. O.; Manne, R.; Baer, Y. "ESCA Applied to Free Molecules"; North-Holland: Amsterdam, 1969.

(16) Hordvik, A.; Rimala, T. S.; Saethre, L. J. *Acta Chem. Scand.* **1972**, *26*, 2139.

(17) (a) Hordvik, A.; Rimala, T. S.; Saethre, L. J. *Acta Chem. Scand.* **1973**, *27*, 360. (b) Hordvik, A.; Porten, J. *Ibid.* **1973**, *27*, 485. (c) Jynge, K. Cand. Real. Thesis, 1976, Department of Chemistry, University of Tromsø, Tromsø, Norway.

(18) Hordvik, A. *Acta Chem. Scand.* **1966**, *20*, 1885.

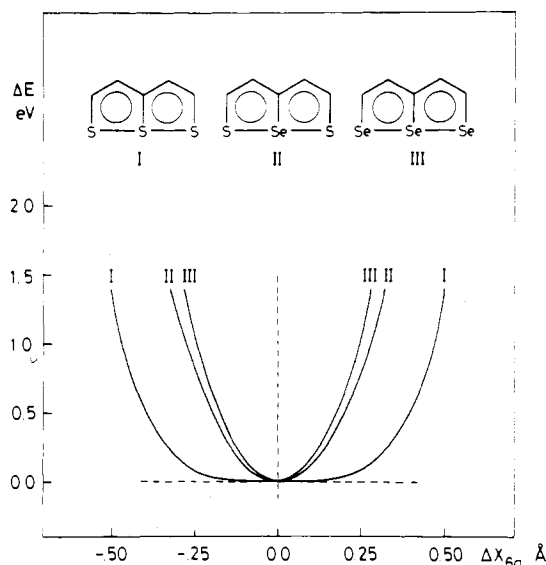


Figure 6. Ground-state potential curves for trithiapentalene (I), dithiaselenapentalene (II), and triselenapentalene (III) as found from CNDO/2 calculations.

Å for C¹⁹ we obtained $R = 1.20$ Å for Se, the same value as found earlier.⁷

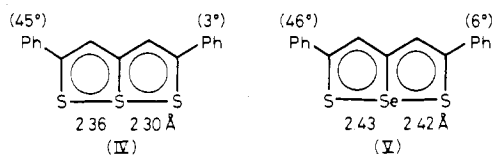
It is seen from eq 2 that the fwhm:s are proportional to the ground-state vibrational amplitude, provided that the line shapes and the slopes of the final states are constant, i.e., eq 4.

$$\text{fwhm} = K\Delta X_G \quad (4)$$

Table II compares K for the three molecules. The agreement is good, and it seems that the approximations are justified for this series of molecules. The reason is probably that all bonds in the three-center sequence of I, II, and III are considerably longer than single bonds. This makes ΔX_G large, and the potential minima for the final states are probably all well outside region I (see Figure 5).

The analysis above indicates that the observed decrease in fwhm is due to a smaller vibrational amplitude for II and III compared to I, or in other words, due to a more narrow ground-state potential for the Se derivatives. This implies that the S-Se and Se-Se bonds are less liable to changes when the molecules are perturbed, e.g., by substituents.²⁰

From the published structural data on Se derivatives, there is one example that supports this prediction. The crystals of 2,5-diphenyl-6a-trithiapentalene (IV)²¹ are isomorphous with those of 2,5-diphenyl-1,6-dithia-6a-selenapentalene (V),¹⁶ and



(19) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N. Y., 1960.

(20) An amplitude decrease could be expected because of the mass increase of the 6a atom. However, since the potential curve for I is believed to be very flat with an energy spacing on the order of kT , the mass contribution is less important and cannot alone explain the observed decrease.

(21) Hordvik, A. *Acta Chem. Scand* **1971**, 25, 1583.

Table III. Comparison of Wiberg Bond Indices,^a Charge (q), and Electron Distribution in π and σ Orbitals for the 1,6a,6 Three-Center Sequence

three-center sequence	$W(1-6a)^a$			1,6		6a			
	tot.	π	σ	q	π	σ	q	π	σ
S-S-S	1.02	0.19	0.83	-0.12	1.79	4.33	-0.03	1.76	4.27
S-Se-S	1.20	0.26	0.94	-0.09	1.76	4.33	-0.05	1.74	4.31
Se-Se-Se	1.23	0.30	0.93	-0.07	1.77	4.30	-0.05	1.70	4.35

^a Bond indices according to Wiberg,²⁶ $W(1-6a) = \sum_{\mu}^1 \sum_{\nu}^{6a} P_{\mu\nu}^2$, where $P_{\mu\nu}$ is the CNDO/2 bond-order matrix element.

the molecular packing is therefore quite similar for the two molecules. The difference in S-S bond lengths in IV is attributed to the different twist angles of the phenyl groups.²² Although the twist angles in V are almost the same as in IV, the S-Se bonds are much less affected, in agreement with the argument above.

A narrower ground-state potential curve for the Se derivatives is also consistent with the results from CNDO/2 calculations, as seen in Figure 6. Ground-state potential energy curves are calculated for the "bell-clapper" motion of the 6a atom. The displacement of the central atom is in each case performed within a fixed molecular framework, which is consistent with the electron diffraction analysis of I.²³ The QCPE 261 program with the original parameters was employed.^{24,25} Figure 6 shows that both Se potentials come out considerably more narrow than for trithiapentalene. Part of this steepness is probably due to the small (Slater's rule) orbital exponent used for Se.²⁵

The results above may be explained from an analysis of the CNDO/2 density matrix for the molecules at their symmetrical equilibrium geometries. Table III shows that the narrowing of the potential curves is accompanied by an increase of the bond strengths, as calculated from the Wiberg²⁶ "bond index" (eq 5), where $P_{\mu\nu}$ is the bond-order matrix element. The

$$W(1-6a) = \sum_{\mu}^1 \sum_{\nu}^{6a} P_{\mu\nu}^2 \quad (5)$$

bond strength increase takes place in σ as well as the π system. Table III shows that the change in bonding properties is experienced as a rearrangement of the charge density, which leads to a decrease in the 1-6a charge separation. For the 6a atom it is interesting to note that the decrease in π electron density is paralleled by an increase in σ density on this atom. This keeps the charge almost constant for the central atom of the three-center sequence.

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Registry No. I, 252-09-5; II, 34115-24-7; III, 35124-80-2.

(22) Hansen, L. K.; Hordvik, A.; Saethre, L. J. *Chem. Commun.* **1972**, 222.

(23) Shen, Q.; Hedberg, K., *J. Am. Chem. Soc.* **1974**, 96, 289.

(24) Quantum Chemistry Program Exchange, No. 261, Chemistry Department, Indiana University, Bloomington, Ind. 47401.

(25) Hase, H. L.; Schweig, A. *Theor. Chim. Acta* **1973**, 31, 215.

(26) Wiberg, K. B. *Tetrahedron* **1968**, 24, 1083.