HOULIHAH, W. J. (1973). *Chem. Abstr.* **79**, 115651m.
IKEMOTO, I., YAKUSHI, K., NAITO, Y., KURUDO, A. & SANO, M. (1977). *Acta Cryst.* B**33**, 2076–2079.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
REYNOLDS, B. & CARSON, J. (1970). *Chem. Abstr.* **72**, 55528v.
ROYCHOWDHURY, P. & BASAK, B. S. (1975). *Acta Cryst.* B**31**, 1559–1563.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHOJA, M. (1988). *Acta Cryst.* C**44**, 2238–2239.
SINDT, A. C. & MACKAY, M. F. (1979). *Acta Cryst.* B**35**, 2452–2454.
VIJAYALAKSHMI, B. K. & SRINIVASAN, R. (1975). *Acta Cryst.* B**31**, 999–1003.
WEI, P. H. L. & STANLEY, C. (1970). *Chem. Abstr.* **73**, 66635z.
WHITE, A. C. & BLACK, R. M. (1976). *Chem. Abstr.* **85**, 177505z.

Acta Cryst. (1991). C**47**, 998–1003

Structures of 6a-Thia/Selena-1,3,4,6-tetraazapentalene Derivatives: Hypervalent S/Se—N Bonds

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Abstract. 2,3,4,5-Tetrahydro-1,6-diphenyl-3,4-propano-6a-thia-1,3,4,6-tetraazapentalene-2,5-dione, (I), $C_{18}H_{16}N_4O_2S$, $M_r = 352{\cdot}42$, orthorhombic, $Iba2$, $a = 20{\cdot}490\,(10)$, $b = 21{\cdot}420\,(5)$, $c = 7{\cdot}575\,(2)$ Å, $V = 3324\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}408$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}204$ mm^{-1}, $F(000) = 1472$, $T = 293$ K, $R = 0{\cdot}051$ for 1014 observed reflections. 1,6-Diethyl-2,3,4,5-tetrahydro-3,4-propano-6a-thia-1,3,4,6-tetraazapentalene-2,5-dione, (II), $C_{10}H_{16}N_4O_2S$, $M_r = 256{\cdot}33$, monoclinic, $P2_1/n$, $a = 23{\cdot}888\,(3)$, $b = 4{\cdot}8422\,(6)$, $c = 22{\cdot}518\,(4)$ Å, $\beta = 102{\cdot}62\,(1)^\circ$, $V = 2541{\cdot}8\,(6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}340$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2{\cdot}214$ mm^{-1}, $F(000) = 1088$, $T = 293$ K, $R = 0{\cdot}073$ for 2615 observed reflections. 1,6-Diethyl-2,3,4,5-tetrahydro-3,4-propano-6a-selena-1,3,4,6-tetraazapentalene-2,5-dithione, (III), $C_{10}H_{16}N_4S_2Se$, $M_r = 335{\cdot}36$, monoclinic, $P2_1$, $a = 13{\cdot}025\,(4)$, $b = 10{\cdot}233\,(1)$, $c = 5{\cdot}2535\,(7)$ Å, $\beta = 98{\cdot}36\,(2)^\circ$, $V = 692{\cdot}7\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}611$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}956$ mm^{-1}, $F(000) = 340$, $T = 293$ K, $R = 0{\cdot}043$ for 1382 observed reflections. Each molecule has approximate mirror symmetry except phenyl or ethyl groups with equidistant S—N/Se—N bonds. The mean distances of S—N bonds are 1·959 (6) and 1·927 (6) Å in (I) and (II), respectively, and that of the Se—N bonds in (III) is 2·034 (6) Å. These values are longer than those of the normal S/Se—N single bonds by 9–12%. The S—C distances, 1·717 (7) for (I), 1·717 (6) Å (mean value) for (II), and the Se—C distance, 1·852 Å for (III), are intermediate between those for single and double bonds. The pentalene framework and O or S atoms of carbonyl or thiocarbonyl groups are almost coplanar. The structural features show the π-hypervalency of the 12π-system.

Introduction. It is well known that the S atom shows hypervalency (Musher, 1969). In typical hypervalent compounds, such as σ-sulfuranes (Paul, Martin & Perozzi, 1972; Kálmán, Sásvári & Kapovits, 1973) and thiathiophthenes (Hansen & Hordvik, 1973), a tetravalent or divalent S atom contacts with electronegative groups, X and Y forming linear $X\cdots S\cdots Y$ bonds. The lengths of the $S\cdots X$ and $S\cdots Y$ bonds are longer than those of S—X and S—Y single bonds and shorter than the sum of the van der Waals radii, and correspond to 0·5 of Pauling's bond order (Pauling, 1960).

Compounds (I), (II) and (III), which have tetraazathia- or tetraazaselenapentalene frames with carbonyl or thiocarbonyl groups, are expected to show hypervalency like that in 6a-thiathiophthenes.

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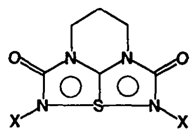
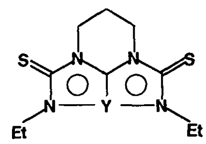
The crystal structures of compounds (I), (II) and (III) have been determined by X-ray diffraction in order to investigate the effects of the carbonyl or thiocarbonyl groups on the π-hypervalent system.



(I) X = Ph
(II) X = Et



(III) Y = Se
(IV) X = S

Experimental. Details of data collection and structure refinement are listed in Table 1. Intensity data were collected using a Rigaku AFC-4 diffractometer with graphite monochromator. For (II) absorption corrections were applied numerically, but not applied to (I) and (III). After failure to solve the structure of (I) by direct methods the structure was solved by the Patterson method using *SHELXS*86 (Sheldrick, 1986). H atoms were found from the difference maps. Block-diagonal least squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized, $w = 1/[\sigma^2(F) + 0{\cdot}00024|F_o|^2]$.

Crystals of (II) are unstable and intensities of monitored reflections decreased to 78% during intensity collection, for which appropriate corrections were made. This structure was also solved by the Patterson method using *SHELXS*86. H atoms except several atoms of the ethyl groups were found from the difference maps. The remaining H atoms were located from the calculation. Block-diagonal least squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. $w = 1/[\sigma^2(F) + 0{\cdot}00400|F_o|^2]$. Four reflections ($\bar{2}02$, 004, 202 and $\bar{4}14$) were omitted from the least-squares refinements. R(refinement) = 0·072, R(observed) = 0·073.

The structure of (III) was solved by direct methods with the program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms except several atoms of ethyl groups were found from the difference maps. The remaining H atoms were located from the calculations. Block-diagonal least squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. $w = 1/(1{\cdot}5172 - 0{\cdot}1212|F_o| + 0{\cdot}0029|F_o|^2)$.

The final atomic parameters are given in Table 2.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on a HITAC M260D Computer of the Data Processing Center of the University of Electro-Communications with the programs *SHELXS*86, *MULTAN*78 and *UNICS*III (Sakurai & Kobayashi, 1979).

Table 1. *Details of data collection and structure refinement*

	(I)	(II)	(III)
Color	Colorless	Colorless	Pale yellow
Crystal shape	Needles	Needles	Plates
Crystal size (mm)	0·10 × 0·10 × 0·40	0·03 × 0·15 × 0·15	0·11 × 0·15 × 0·65
2θ range for cell parameters (°)	27·2–33·5	59·8–73·6	29·7–34·7
Number of reflections	24	21	25
Scan range 2θ(°)	2–55	2–130	2–55
Scan width $\Delta\omega$ (°)	$1{\cdot}4 + 0{\cdot}4\tan\theta$	$1{\cdot}2 + 0{\cdot}4\tan\theta$	$1{\cdot}2 + 0{\cdot}5\tan\theta$
Scan speed 2θ (° min^{-1})	4	4	4
Scan mode	2θ–ω	2θ–ω	2θ–ω
Monitored reflections (every 50 reflections)	202, 080, $6\bar{2}0$	$12\bar{8}$, 11,0,3 $90\bar{9}$	$\bar{4}02$, $\bar{1}30$, 410
Variation of intensities	0·990–1·013	0·780–1·003	0·994–1·005
Range of h,k,l	−28–28,0–27,0–9	−28–28, −5–0,0–26	−16–16,0–13,0–6
Time for background (s)	10	10	10
Transmission factor $A_{\max}$–$A_{\min}$		0·957–0·754	
Number of reflections			
Measured	4375	4683	1967
Unique, $R_{\rm int}$	2355, 0·028	4294, 0·023	1847, 0·027
Observed [$\lvert F_o\rvert > 3\sigma(F)$]	1014	2615	1382
R	0·051	0·073	0·043
wR	0·042	0·081	0·039
$\Delta\rho_{\max}$ (e Å^{-3})	0·41	0·56	0·87
$(\Delta/\sigma)_{\max}$	0·052	0·082	0·192
S	1·218	1·555	1·037

Discussion. The molecular structures with the atomic numbering are shown in Fig. 1. Bond distances and angles are listed in Table 3.

Molecular structures of (I) *and* (II). In crystals of (II), there are two independent molecules, *A* and *B*, which are chemically equivalent. Each molecule of (I) and (II) has approximate mirror symmetry except for the phenyl groups of (I). The mean S—N distances are 1·959 for (I) and 1·927 Å for (II). Each tetraazathiapentalene framework is almost planar within the maximum deviations 0·081 (6), 0·032 (5) and 0·008 (5) Å for (I), (II*A*) and (II*B*), respectively. The exocyclic atoms bonded directly to the pentalene frameworks also lie on the same planes within 0·176 (9), 0·106 (6) and 0·045 (9) Å for (I), (II*A*) and (II*B*), respectively. The slightly worse planarity for (I) than for (II) can be seen from some torsion angles. For N(1)—C(2)—N(3)—C(3) and N(6)—C(5)—N(4)—C(3) the torsion angles are: (I) 6·5 (7), −3·7 (7), (II*A*) −2·3 (6), 2·8 (6), (II*B*) 0·2 (6), 0·5 (6)°, respectively. For O(2)—C(2)—N(1)—C(11) and O(5)—C(5)—N(6)—C(21) they are: (I) 9·6 (9), 9·9 (9), (II*A*) 1·9 (8), 1·3 (8), (II*B*) 2·0 (7), 0·2 (8)°, respectively. For (I) the dihedral angles between the pentalene plane and the phenyl groups are 45·6 (2) and 28·6 (2)°. For (II) the two terminal methyl groups, C(12) and C(22), are located on the opposite side from C(7) of the central methylene group as shown in Fig. 1(*d*). In the case of 2,3,4,5-tetrahydro-

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, H-atom parameters, and bond lengths and angles related to H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53486 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters and equivalent isotropic temperature factors* (Å^2) *for non*-H *atoms*

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I) (× 10^5 for S, × 10^4 for others)				
S(1)	13700 (8)	19186 (8)	50158 (29)	3·13 (4)
O(2)	1917 (2)	2741 (2)	9503 (7)	4·67 (16)
O(5)	2413 (2)	475 (2)	3207 (7)	4·63 (16)
N(1)	1342 (3)	2523 (3)	6939 (7)	3·80 (16)
N(3)	2150 (3)	1891 (2)	7752 (8)	3·51 (16)
N(4)	2311 (2)	1118 (2)	5631 (7)	2·98 (15)
N(6)	1614 (3)	1245 (2)	3375 (7)	3·30 (16)
C(2)	1795 (3)	2453 (3)	8157 (9)	3·31 (19)
C(3)	2001 (3)	1614 (3)	6234 (9)	2·68 (18)
C(5)	2116 (3)	897 (3)	3927 (10)	3·17 (19)
C(6)	2686 (4)	1664 (3)	8876 (11)	4·71 (24)
C(7)	2793 (4)	979 (4)	8504 (12)	5·91 (28)
C(8)	2877 (3)	842 (3)	6571 (11)	3·88 (21)
C(11)	922 (3)	3053 (3)	6853 (10)	3·82 (21)
C(12)	274 (3)	2954 (3)	6366 (11)	4·90 (25)
C(13)	−145 (4)	3464 (4)	6248 (13)	6·16 (30)
C(14)	53 (6)	4042 (3)	6606 (14)	7·09 (31)
C(15)	694 (5)	4149 (3)	7095 (13)	6·45 (31)
C(16)	1129 (3)	3661 (3)	7234 (11)	4·73 (24)
C(21)	1245 (3)	1122 (3)	1829 (9)	2·88 (19)
C(22)	1176 (3)	519 (3)	1155 (11)	4·20 (23)
C(23)	783 (4)	410 (3)	−302 (11)	4·92 (25)
C(24)	469 (3)	894 (4)	−1118 (11)	5·39 (26)
C(25)	541 (3)	1492 (4)	−470 (10)	4·38 (23)
C(26)	928 (3)	1597 (3)	992 (9)	3·77 (22)
(II) (× 10^5 for S, × 10^4 for others)				
S(1*A*)	11255 (6)	−15015 (37)	−11649 (7)	4·92 (5)
O(2*A*)	2683 (1)	1223 (9)	−366 (2)	5·33 (13)
O(5*A*)	−255 (1)	1504 (8)	−677 (2)	4·91 (12)
N(1*A*)	1946 (2)	−1184 (12)	−1001 (2)	5·31 (16)
N(3*A*)	1732 (2)	1676 (9)	−315 (2)	3·79 (12)
N(4*A*)	731 (2)	1785 (9)	−428 (2)	3·63 (12)
N(6*A*)	329 (2)	−1150 (11)	−1156 (2)	5·30 (15)
C(2*A*)	2189 (2)	525 (12)	−566 (2)	4·28 (17)
C(3*A*)	1203 (2)	864 (11)	−583 (2)	3·53 (15)
C(5*A*)	206 (2)	709 (12)	−764 (2)	3·98 (16)
C(6*A*)	1839 (2)	3538 (12)	211 (2)	4·24 (16)
C(7*A*)	1339 (2)	3349 (13)	519 (2)	4·65 (17)
C(8*A*)	772 (2)	3753 (12)	84 (2)	4·28 (16)
C(11*A*)	2288 (3)	−2794 (17)	−1350 (3)	7·10 (25)
C(12*A*)	2435 (5)	−1192 (25)	−1833 (5)	13·36 (52)
C(21*A*)	−109 (3)	−2642 (16)	−1593 (3)	6·00 (21)
C(22*A*)	−357 (4)	−921 (17)	−2117 (3)	9·23 (32)
S(1*B*)	42479 (6)	13378 (35)	15635 (7)	4·48 (4)
O(2*B*)	5432 (1)	−1359 (9)	694 (2)	5·08 (12)
O(5*B*)	2645 (1)	−1491 (9)	1100 (2)	5·66 (13)
N(1*B*)	4998 (2)	1044 (11)	1367 (2)	4·90 (15)
N(3*B*)	4475 (2)	−1931 (9)	711 (2)	3·51 (12)
N(4*B*)	3533 (2)	−1990 (9)	851 (2)	3·73 (12)
N(6*B*)	3450 (2)	941 (11)	1593 (2)	4·98 (15)
C(2*B*)	5032 (2)	−703 (12)	921 (2)	3·99 (16)
C(3*B*)	4072 (2)	−1074 (12)	997 (2)	3·66 (15)
C(5*B*)	3151 (2)	−814 (13)	1206 (3)	4·70 (18)
C(6*B*)	4346 (2)	−3874 (12)	207 (2)	4·22 (16)
C(7*B*)	3718 (2)	−3657 (13)	−102 (2)	4·38 (16)
C(8*B*)	3341 (2)	−3998 (12)	363 (3)	4·29 (16)
C(11*B*)	5498 (3)	2650 (15)	1667 (3)	5·97 (21)
C(12*B*)	5871 (3)	1123 (20)	2170 (4)	9·76 (33)
C(21*B*)	3184 (3)	2557 (16)	2011 (3)	6·23 (22)
C(22*B*)	3216 (3)	1012 (19)	2604 (3)	8·07 (29)
(III) (× 10^5 for Se, × 10^4 for others)				
Se	33883 (4)	35368 (14)	14408 (12)	3·71 (1)
S(2)	3856 (2)	6739 (2)	−4171 (4)	5·45 (6)
S(5)	503 (1)	3618 (3)	5301 (3)	5·25 (5)
N(1)	4039 (4)	4596 (6)	−1153 (11)	4·03 (15)
N(3)	2602 (4)	5773 (5)	−928 (10)	3·55 (14)
N(4)	1585 (4)	4816 (6)	1932 (10)	3·54 (14)
N(6)	2314 (4)	2984 (6)	3708 (11)	3·99 (15)
C(2)	3532 (5)	5630 (7)	−2009 (12)	3·74 (17)
C(3)	2418 (5)	4861 (6)	740 (12)	3·37 (16)
C(5)	1511 (4)	3733 (11)	3659 (12)	3·83 (19)
C(6)	1869 (6)	6864 (8)	−1549 (14)	4·61 (20)
C(7)	1265 (6)	7072 (8)	679 (14)	4·82 (22)
C(8)	768 (5)	5815 (8)	1379 (13)	4·42 (20)
C(11)	5040 (6)	4207 (10)	−1840 (15)	5·49 (23)
C(12)	5907 (7)	4793 (11)	−83 (20)	7·25 (33)
C(21)	2461 (6)	1764 (9)	5182 (14)	5·01 (22)
C(22)	1851 (7)	643 (9)	3892 (18)	6·12 (27)

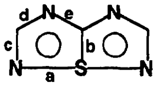
Table 3. *Bond lengths* (Å) *and angles* (°) *of non*-H *atoms*

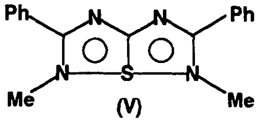
For (III) S(1), O(2) and O(5) denote Se, S(2) and S(5), respectively.

	(I)	(II*A*)	(II*B*)	(III)
S(1)—N(1)	1·949 (6)	1·920 (6)	1·943 (5)	2·022 (6)
S(1)—N(6)	1·969 (6)	1·914 (6)	1·932 (5)	2·045 (6)
S(1)—C(3)	1·717 (7)	1·720 (6)	1·713 (6)	1·852 (7)
O(2)—C(2)	1·217 (9)	1·217 (7)	1·221 (7)	1·702 (8)
O(5)—C(5)	1·220 (9)	1·223 (7)	1·225 (8)	1·676 (12)
N(1)—C(2)	1·318 (9)	1·316 (8)	1·330 (8)	1·293 (9)
N(1)—C(11)	1·426 (9)	1·474 (10)	1·460 (9)	1·457 (12)
N(3)—C(2)	1·441 (9)	1·446 (7)	1·439 (7)	1·418 (9)
N(3)—C(3)	1·329 (9)	1·334 (7)	1·334 (7)	1·326 (9)
N(3)—C(6)	1·473 (10)	1·467 (7)	1·455 (7)	1·474 (10)
N(4)—C(3)	1·318 (9)	1·329 (7)	1·334 (7)	1·331 (9)
N(4)—C(5)	1·432 (9)	1·414 (7)	1·454 (8)	1·445 (13)
N(4)—C(8)	1·486 (10)	1·483 (7)	1·464 (7)	1·473 (10)
N(6)—C(5)	1·337 (9)	1·337 (8)	1·311 (8)	1·294 (13)
N(6)—C(21)	1·417 (9)	1·462 (9)	1·470 (9)	1·467 (11)
C(6)—C(7)	1·510 (12)	1·510 (9)	1·514 (8)	1·518 (11)
C(7)—C(8)	1·503 (12)	1·501 (8)	1·532 (8)	1·509 (11)
C(11)—C(12)	1·392 (11)	1·439 (15)	1·476 (12)	1·477 (15)
C(11)—C(16)	1·400 (11)			
C(12)—C(13)	1·392 (13)			
C(13)—C(14)	1·330 (15)			
C(14)—C(15)	1·383 (15)			
C(15)—C(16)	1·379 (13)			
C(21)—C(22)	1·397 (11)	1·461 (12)	1·518 (12)	1·500 (13)
C(21)—C(26)	1·364 (10)			
C(22)—C(23)	1·387 (12)			
C(23)—C(24)	1·368 (12)			
C(24)—C(25)	1·379 (12)			
C(25)—C(26)	1·380 (10)			
N(1)—S(1)—N(6)	165·0 (3)	165·0 (3)	165·3 (2)	158·5 (2)
N(1)—S(1)—C(3)	82·7 (3)	82·2 (3)	82·5 (3)	79·3 (3)
N(6)—S(1)—C(3)	82·5 (3)	82·8 (3)	82·8 (3)	79·2 (3)
S(1)—N(1)—C(2)	115·3 (5)	117·2 (4)	115·4 (4)	115·5 (5)
S(1)—N(1)—C(11)	120·8 (5)	121·1 (5)	123·9 (4)	119·9 (5)
C(2)—N(1)—C(11)	123·1 (6)	121·6 (6)	120·7 (5)	124·6 (7)
C(2)—N(3)—C(3)	116·2 (6)	115·5 (5)	115·2 (5)	116·0 (6)
C(2)—N(3)—C(6)	121·9 (6)	122·6 (5)	123·0 (4)	123·6 (6)
C(3)—N(3)—C(6)	121·6 (6)	121·8 (5)	121·7 (5)	120·4 (6)
C(3)—N(4)—C(5)	116·4 (6)	116·1 (5)	115·0 (5)	117·1 (7)
C(3)—N(4)—C(8)	122·1 (6)	120·3 (4)	122·1 (5)	119·9 (6)
C(5)—N(4)—C(8)	121·2 (6)	123·6 (4)	122·8 (5)	123·0 (7)
S(1)—N(6)—C(5)	113·9 (5)	115·4 (4)	116·0 (4)	116·4 (6)
S(1)—N(6)—C(21)	121·5 (4)	121·1 (4)	122·5 (4)	119·7 (5)
C(5)—N(6)—C(21)	124·4 (6)	123·2 (6)	121·4 (5)	123·9 (7)
O(2)—C(2)—N(1)	132·3 (7)	133·1 (6)	131·5 (6)	127·9 (6)
O(2)—C(2)—N(3)	120·0 (6)	120·2 (5)	120·6 (5)	120·5 (5)
N(1)—C(2)—N(3)	107·5 (6)	106·7 (5)	107·9 (5)	111·6 (6)
S(1)—C(3)—N(3)	117·9 (5)	118·3 (4)	119·1 (4)	117·6 (5)
S(1)—C(3)—N(4)	118·8 (5)	117·9 (4)	118·4 (4)	117·5 (5)
N(3)—C(3)—N(4)	123·3 (6)	123·8 (5)	122·5 (5)	124·9 (6)
O(5)—C(5)—N(4)	120·6 (6)	121·5 (5)	120·0 (5)	120·4 (8)
O(5)—C(5)—N(6)	131·1 (7)	130·8 (6)	132·3 (6)	129·7 (9)
N(4)—C(5)—N(6)	108·2 (6)	107·7 (5)	107·7 (5)	109·8 (9)
N(3)—C(6)—C(7)	108·7 (6)	108·5 (5)	109·5 (5)	109·1 (6)
C(6)—C(7)—C(8)	112·9 (7)	112·6 (5)	110·4 (5)	110·9 (6)
N(4)—C(8)—C(7)	107·4 (6)	108·7 (5)	108·0 (5)	108·5 (6)
N(1)—C(11)—C(12)	117·8 (7)	111·9 (8)	112·5 (6)	111·4 (8)
N(1)—C(11)—C(16)	123·3 (7)			
C(12)—C(11)—C(16)	119·0 (7)			
C(11)—C(12)—C(13)	119·1 (8)			
C(12)—C(13)—C(14)	121·8 (9)			
C(13)—C(14)—C(15)	120·0 (10)			
C(14)—C(15)—C(16)	120·5 (9)			
C(11)—C(16)—C(15)	119·6 (8)			
N(6)—C(21)—C(22)	121·8 (6)	111·5 (7)	110·8 (6)	113·1 (7)
N(6)—C(21)—C(26)	120·0 (6)			
C(22)—C(21)—C(26)	118·1 (7)			
C(21)—C(22)—C(23)	120·4 (7)			
C(22)—C(23)—C(24)	120·3 (8)			
C(23)—C(24)—C(25)	119·6 (8)			
C(24)—C(25)—C(26)	119·9 (7)			
C(21)—C(26)—C(25)	121·7 (7)			

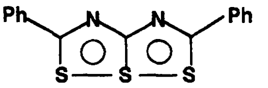
1,6-diethyl-3,4-propano-6a-thia-1,3,4,6-tetraazapentalene-2,5-dithione (IV) (Matsumura, Tomura, Yoneda & Toriumi, 1986) the two methyl groups are on either side of the pentalene plane like those in (III) (Fig. 1*d*). The torsion angles about the ethyl groups S(1)—N(1)—C(11)—C(12) and S(1)—N(6)—C(21)—C(22) are 98·2 (7) and −95·9 (6)°, respectively in (II*A*) and 96·1 (6) and −92·1 (6)°, respectively in (II*B*).

Molecular structure of (III). The lengths of the Se—N bonds are 2·022 (6) and 2·045 (6) Å. The C=S lengths, 1·702 (8) and 1·676 (12) Å, are clearly longer than the normal length of a C=S double bond (1·61 Å). The corresponding values of (IV) are 1·683 and 1·674 Å. The planarity of the pentalene framework is better than that of (I). The maximum deviation of the defined atoms is 0·018 (5) Å and that of exocyclic atoms bonded to the pentalene framework is 0·093 (10) Å [C(21)]. The locations of the terminal methyl groups are the same as those for (IV). The torsion angles of Se—N—C—C for ethyl groups are −88·0 (7) and −98·4 (6)°.

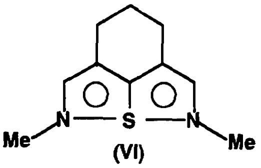




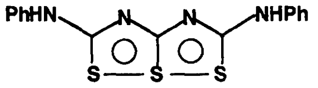
(V)



(VII)



(VI)



(VIII)

The geometry of the pentalene framework. The average distances of the bonds in the tetraazathiapentalene frameworks are summarized in

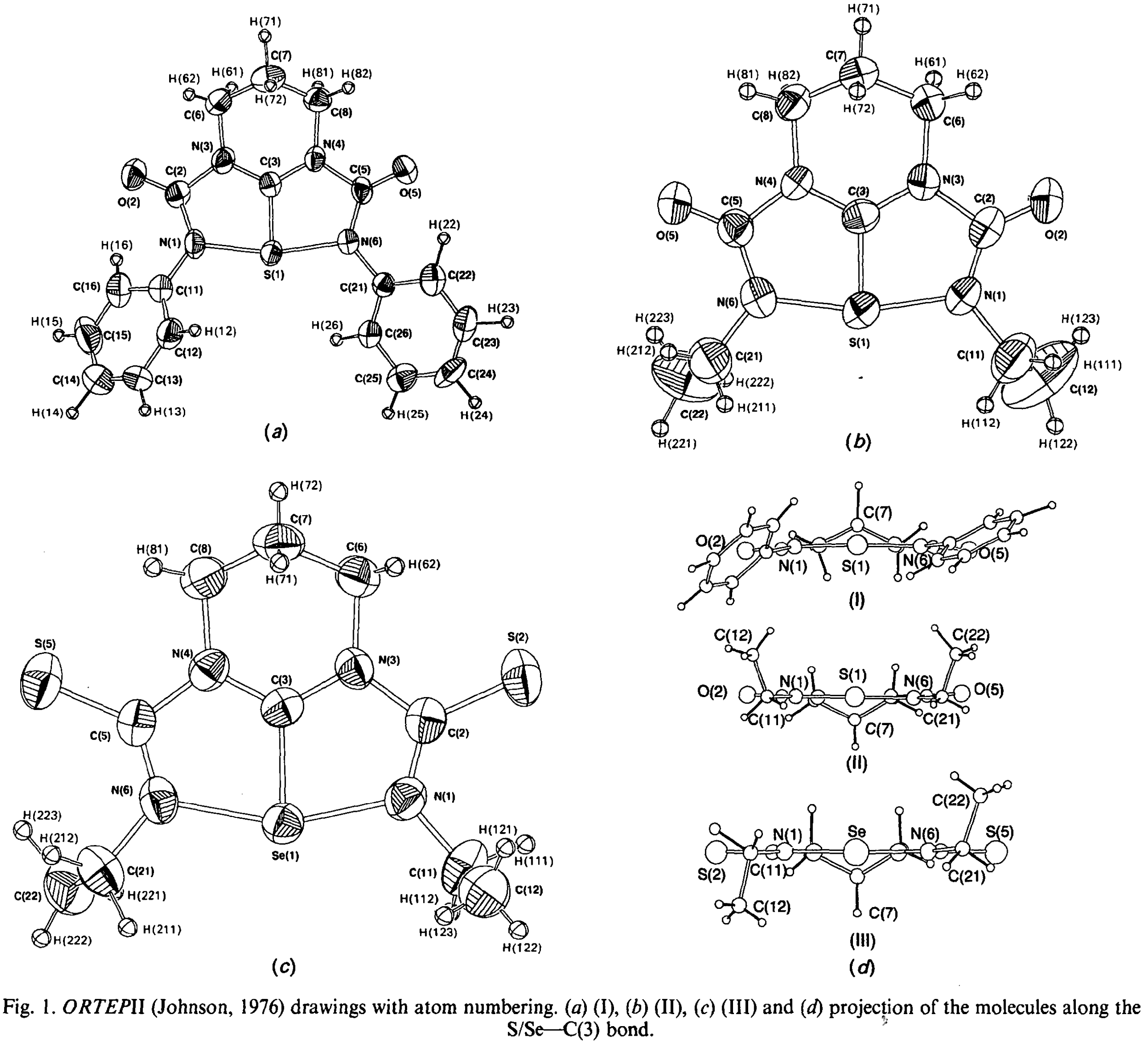


Fig. 1. *ORTEP*II (Johnson, 1976) drawings with atom numbering. (*a*) (I), (*b*) (II), (*c*) (III) and (*d*) projection of the molecules along the S/Se—C(3) bond.

Table 4, together with those of related compounds. The S—N distances in (I) and (II) are longer than that of the normal S—N single bond (1·74 Å) by 10–12%, but shorter than the sum of the van der Waals radii of S and N (3·35 Å). In the case of (IV), 3,4-dimethyl-2,5-diphenyl-3,4-dihydro-3a-thia-1,3,4,6-tetraazapentalene (V) (Iwasaki & Akiba, 1984) and 3,4-dihydro-1,6-dimethyl-3,4-propano-6a-thia-1,6-diazapentalene (VI) (Hordvik & Julshamn, 1972) the S—N distances are 1·909, 1·904 and 1·925 Å, respectively. The longer S—N distances and the worse planarity observed in (I) than in (II) are considered to be due to the bulky substituents at the 1- and 6-positions. The average distance of the Se—N bond (2·034 Å) in (III) is longer than that of the normal Se—N single bond (1·87 Å) by 9%. These values and the planarity of the pentalene frameworks of (I), (II) and (III) [and also (IV)] show the π-hypervalency of S and Se atoms in these compounds.

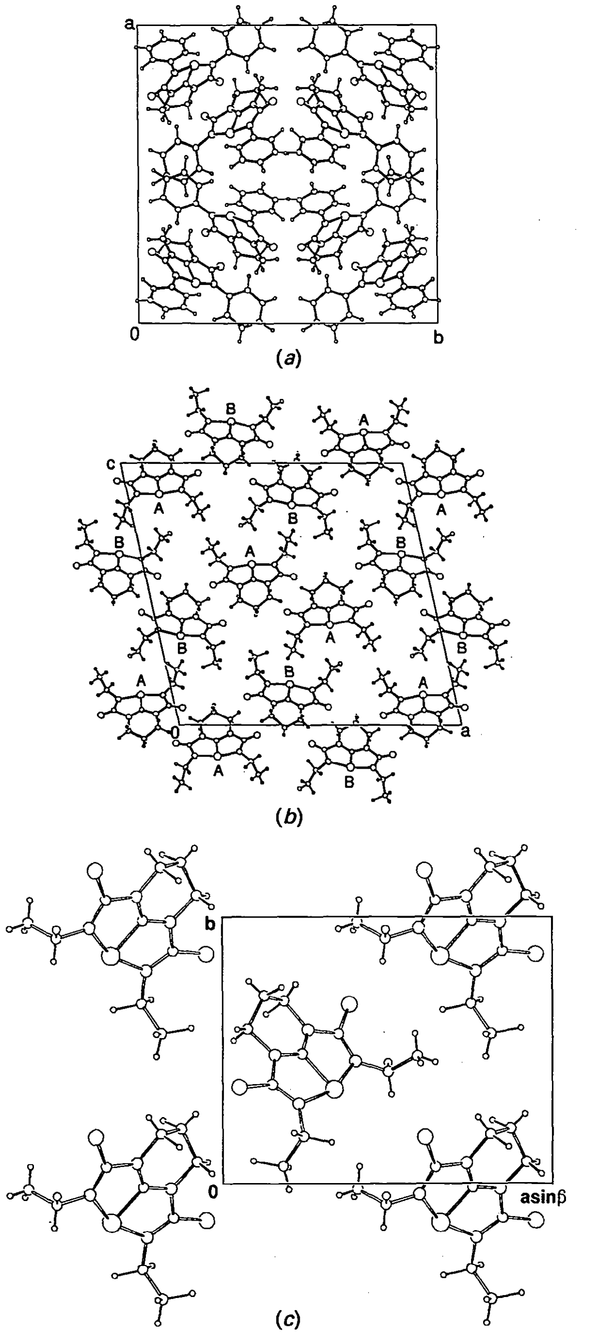


Fig. 2. (*a*) Projection of the crystal structure of (I) viewed along the *c* axis. (*b*) Projection of the crystal structure of (II) viewed along the *b* axis. (*c*) Projection of the crystal structure of (III) viewed along the *c* axis.

The lengths of the other bonds in the pentalene framework are different from the corresponding lengths in (V) and (VI) because of the presence of the carbonyl or thiocarbonyl groups at the 2- and 5-positions. The S—C distances, 1·717 and 1·717 Å in (I) and (II), respectively, are between single- and double-bond lengths. In (IV) the corresponding length is 1·705 Å, while in (V) and (VI) it is 1·764, 1·742 Å, respectively. The N—C *c* distances [N(1)—C(2) and N(6)—C(5)] are almost same as the values for (I)–(VI), showing the double-bond character. On the other hand the *d* and *e* distances of (I)–(IV) are quite different from the corresponding distances of (V), 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene (VII) (Hordvik & Milje, 1973) and 2,5-dianilino-3,4-diaza-1,6,6a-trithiapentalene (VIII) (Hordvik & Oftedal, 1981). In most 6a-thiathiophthenes (Hansen & Hordvik, 1973) the inner bond, *e*, is longer than the outer bond, *d*; however, *e* is shorter than *d* in (I)–(IV). This feature is attributed to the effect of the carbonyl or thiocarbonyl groups. The C=O distances in (I) and (II) show the normal double-bond character, while C=S lengths in (III) and (IV) are longer than those of the normal double bond. This corresponds to the slightly shorter lengths of *c* in (III) and (IV) rather than those of (I) and (II). These structural features suggest the contribution of the limiting structures as shown below.

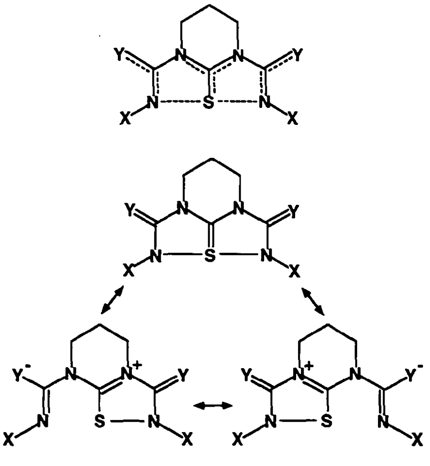


Table 4. *Dimensions* (Å) *of pentalene frameworks*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
a(S—N)	1·959	1·927	2·034^{A}	1·909	1·904	1·925	2·321^{D}	2·350^{D}
b(S—C)	1·717	1·717	1·852^{B}	1·705	1·764	1·742	1·784	1·789
c(N—C)	1·328	1·324	1·294	1·300	1·316	1·328	1·694^{E}	1·711^{E}
d(N—C)	1·437	1·438	1·432	1·423	1·354	1·363^{C}	1·328	1·340
e(N—C)	1·324	1·333	1·329	1·333	1·336	1·398^{C}	1·336	1·329

A: Se—N *B*: Se—C *C*: C—C *D*: S—S *E*: S—C

Crystal structures. The crystal structures are shown in Fig. 2. In the structure of (I) an intermolecular distance shorter than that of the van der Waals contact is 2·924 (9) Å of O(2)···C(3^{i}) [(i): $\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$]. Two independent molecules, *A* and *B*, of (II) are related by a pseudo center of symmetry. Intermolecular distances only slightly shorter than the van der Waals contact are 3·065 (7) Å in O(2*A*)···C(8*B*^{i}) [(i): *x*, *y* + 1, *z*] and 3·050 (7) Å in O(5*A*)···C(8*A*^{ii}) [(ii): $-x$, $1-y$, $-z$]. The structure of (III) is isomorphous with that of (IV). There are no intermolecular distances shorter than the van der Waals distances. The packing mode of (III) and (IV) is quite different from that of (II) as shown in Fig. 2.

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References

HANSEN, L. K. & HORDVIK, A. (1973). *Acta Chem. Scand.* **27**, 411–420.

HORDVIK, A. & JULSHAMN, K. (1972). *Acta Chem. Scand.* **26**, 343–354.

HORDVIK, A. & MILJE, L. M. (1973). *Acta Chem. Scand.* **27**, 510–514.

HORDVIK, A. & OFTEDAL, P. (1981). *Acta Chem. Scand. Ser A*, **35**, 663–668.

IWASAKI, F. & AKIBA, K. (1984). *Bull. Chem. Soc. Jpn*, **57**, 2581–2583.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KÁLMÁN, A., SÁSVÁRI, K. & KAPOVITS, I. (1973). *Acta Cryst.* B**29**, 355–357.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MATSUMURA, N., TOMURA, M., YONEDA, S. & TORIUMI, K. (1986). *Chem. Lett.* pp. 1047–1050.

MUSHER, J. I. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 54–68; *Angew. Chem.* **81**, 68–83.

PAUL, I. C., MARTIN, J. C. & PEROZZI, E. F. (1972). *J. Am. Chem. Soc.* **94**, 5010–5017.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–74.

SHELDRICK, G. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1991). C**47**, 1003–1005

Structure of Tris(2,6-dimethoxyphenyl)phosphine

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Abstract. $C_{24}H_{27}O_6P$, $M_r = 442\cdot45$, *Pbca*, orthorhombic, $a = 7\cdot615\,(3)$, $b = 20\cdot087\,(8)$, $c = 29\cdot447\,(10)$ Å, $V = 4507$ Å^3, $Z = 8$, $D_x = 1\cdot304$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 13\cdot79$ cm^{-1}, $F(000) = 1872$, $T = 295$ K, $R = 0\cdot0568$ for 3067 unique reflections. P—C bond lengths (av. = 1·844 Å) are slightly elongated relative to those of triphenylphosphine (av. = 1·828 Å). C—P—C bond angles (av. = 104·4°) are only slightly larger than those of triphenylphosphine (av. = 103·0°). The plane of one aromatic ring is roughly perpendicular to the plane defined by the three C atoms bound to the P atom while the other two rings are tilted.

Introduction. Tris(2,6-dimethoxyphenyl)phosphine, (1), has been reported (Wada & Higashizaki, 1984) to have very high basicity ($pK_a \simeq 10$) as compared to ordinary triarylphosphines [*e.g.* Ph_3P, pK_a 2·7 (Henderson & Streuli, 1960)]. In addition to enhanced Brønsted basicity, (1) possesses very strong Lewis basicity. It reacts with CH_2Cl_2 rapidly at room temperature to give the chloromethylphosphonium chloride; by contrast triphenylphosphine may be kept in CH_2Cl_2 for extended periods. Wada & Higashizaki (1984) referred to the phosphine's aryl groups as 'bulky' and suggested that, in part, its unusual reactivity might be attributable to *B*-strain. Thus it was of interest to determine the structure of (1).

Experimental. Colorless prisms, 0·25 × 0·20 × 0·20 mm, were obtained by slow evaporation of an